

# Colloidal Hematite Cubes: Magnetic Properties and Self-Assembly

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Cubic hematite particles carry a unique combination of magnetic, optical and catalytic properties that sets them apart from any other colloidal model systems. Thanks to these distinctive traits, hematite cubes have been vital tools to study the physics of several self-assembling systems [1-3].

In this talk I will present an in-depth study of the magnetic properties of micron-sized hematite cubes. First, I will discuss how we experimentally determined the magnitude and the exact spacial orientation of the particle's magnetic dipole moment, and how these values explain the microscopic behavior of the system. Then, I will describe how the particles dipolar interactions can be precisely tuned by growing silica shells of controlled thickness on the hematite surface. Furthermore, I will compare our experimental findings with some recent computer simulation studies, developed upon existing works [4,5], where various self-assembly scenarios were systematically investigated.

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# Macromolecule-Linked Nanoassemblies Designed for Robust SERS

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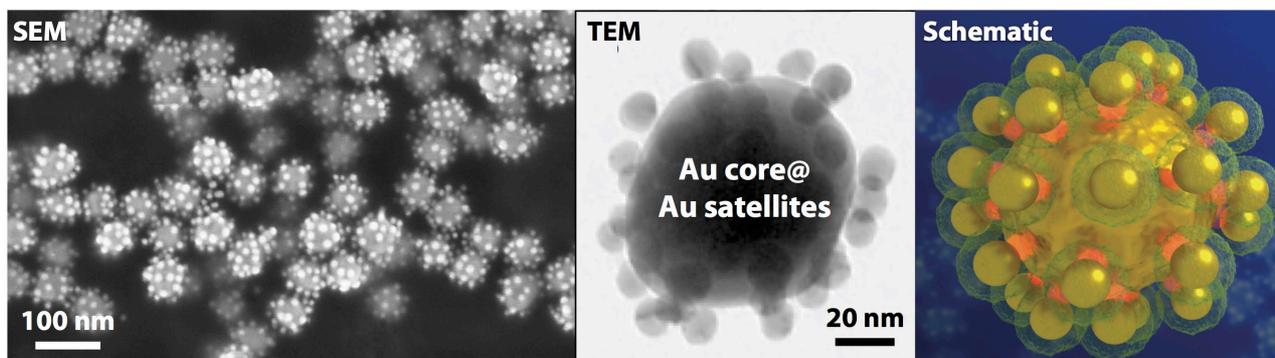
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The use of (bio)macromolecular ligands allows the controlled fabrication of self-assembled 3D nanostructured materials [1]. Especially the control of interparticle distances and relative orientations yields materials with correlated optical and structural properties by design. In this context, we present the retrieval of molecular information at nanoparticle (NP) surfaces using surface-enhanced Raman scattering (SERS). We studied the ligand corona in dispersion and the quantitative exchange of low-molecular-weight surfactants against high-molecular-weight proteins [2]. Individual NPs can be used for the chemical characterization of the surface near-field but SERS enhancement is strongly limited.

Increased enhancement can be achieved by macromolecule-linked NP assemblies (*e.g.*, **Fig. 1**) [3]. We report different synthetic approaches using either synthetic polymer- or biomacromolecule-assisted assembly routes. For benchmarking, the low-molecular-weight analyte 4MBA was detected within the interparticle gaps despite the broad spectral fingerprint of the biomolecules. The limit of detection was determined using non-enhanced volume-Raman signals of the medium as reference.

For bioapplication of such nanoassemblies, besides the robustness SERS enhancement, the aspects of biocompatibility, cellular uptake, and biological are decisive for a rational material design.



**Fig. 1.** Self-assembled nanoassemblies of small gold nanoparticles (16 nm) as satellites on larger gold nanoparticles (84 nm) as cores.

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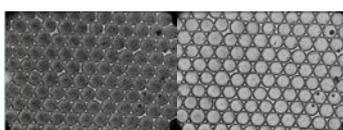
# Bioinspired Composite Materials with Stimuli-Responsive Color Changing Ability

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The ability of changing colors is one of the most exciting features of advanced living organisms. Octopuses, chameleons, squids, all possess cells that can alter their colors. In some cases, the color changing mechanism is due to the ability of these cells to displace pigments over different areas, as in the case of chromatophores in the octopus. In other cases, the change in color is due to a change in the spacing of colloidal crystals, as in the chameleon iridophores. Inspired by this ability, we present here composite materials, consisting of a polymer matrix (PMMA or fluorinated acrylates) containing water droplets. These droplets, with a size of tens of micrometers, contains different responsive particles. When magnetic colloids are incorporated, the application of magnetic field gradients will lead to a displacement of the colloids, similar to the displacement of pigments in chromatophores. When instead temperature-responsive PNIPAm microgels are incorporated into the droplets, at sufficiently high volume fraction they will form colloidal crystals. These crystals create iridescent colors because of the length of the spacing between particles interfering with light. Because the size of the microgels are temperature responsive, the colloidal crystals can be destroyed at a temperature higher than the lower critical solubility temperature, leading to a change in color. Additional stimuli-responsive particles can be used to induce different stimuli-responsive color-changing mechanisms. The proposed approach is thought to be a novel design for stimuli-responsive composite materials with color-changing ability.



*Figure 1- Droplets containing magnetic nanoparticles, without magnetic field (left), in magnetic field (right)*



*Figure 2- Temperature response of PNIPAm microgels*

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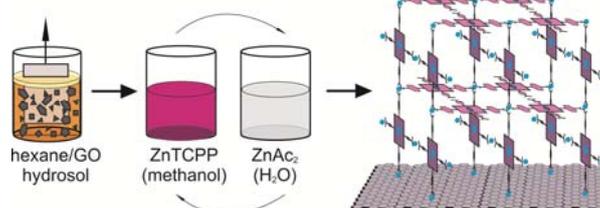
# Porphyrin-Based Metal-Organic Frameworks on Solid-Supported Graphene Oxide Templates

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Metal-organic frameworks on solid surfaces (SURMOFs) are a new class of solid-integrated porous materials, which offer extraordinary properties for sensing, catalysis and molecular electronics. We developed a method for preparation of composite of graphene oxide (GO) and zinc tetra-substituted porphyrin SURMOFs, which is potentially useful as synergetic catalyst, on planar solids. [1, 2] The SURMOF films were assembled via layer-by-layer coordination of zinc pyridyl- and carboxyl-substituted porphyrins with ZnAc<sub>2</sub> clusters on the ultrathin surface coatings of GO. The template GO monolayers were prepared through entropy-driven self-assembly at the hexane/water interface. Microwave autocatalytic reduction was for the first time applied to produce extended surface coatings of highly reduced GO. UV-vis spectroscopy provided evidence for a stepwise assembly of the deposited SURMOF films on these GO films. By using a combination of X-ray and microscopy methods, we found that the resulting GO-associated SURMOFs exhibit leaflet-like planar morphologies with the out-of-plane periodicity different from that of synthetic bulk materials with similar composition. The electrochemical studies showed a synergistic catalytic response of the hybrid structures. Our method offers a route to generate new types of nanocomposites as solid-immobilized membranes and synergistic photocatalytic surface coatings using the GO monolayers as growth-guiding scaffolds.



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# Asymmetric gold superstructures: In situ growth of spherical gold nanoparticles onto the surface of gold nanotriangles

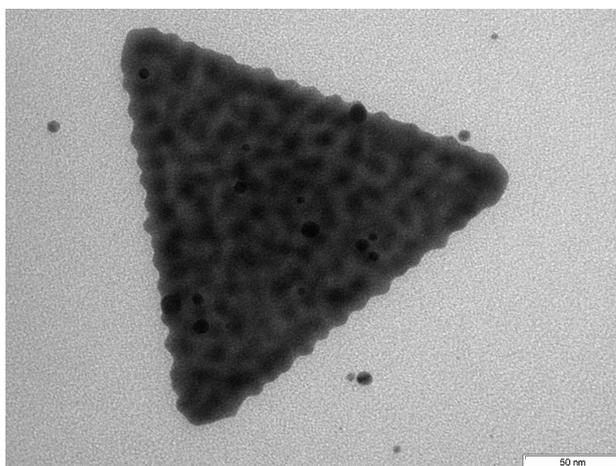
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Asymmetric gold nanocrystals possess unique optical properties and are valuable for many applications in different fields, e.g., in catalysis and medicine. Our one-step synthesis via an Ostwald ripening growth mechanism inside of giant mixed AOT/phospholipid vesicles leads to a spectrum of isotropic and anisotropic particles [1]. The yield of anisotropic gold nanoplatelets can be increased up to almost 100% and the polydispersity can be decreased down to 10% by using a shape-controlled depletion flocculation process in presence of polyelectrolytes and an excess of AOT micelles [2]. The purified gold nanotriangles (NTs), single crystalline face-centered cubic (fcc) structured with twin planes parallel to the (111) direction, produce promising results in vibration experiments by ultrafast X-ray diffraction [3]. These negatively charged, AOT-stabilized NTs with a platelete thickness of about 7 nm and an edge length of about 175 nm can be reloaded by adding poly(ethylene imines) (PEI). In presence of a gold chloride solution and heating up the system to 100 °C, gold clusters are formed in the PEI shell, which grow up to particle dimensions of about 6 nm onto the surface of the nanoplatelets. TEM micrographs show nanotriangle superstructures with embedded spherical gold nanoparticles (Figure 1). These NTs with an undulated crystal surface can be used as a building block for self-assembled layer-by-layer structures with oppositely charged nanotriangles.



**Figure 1** TEM micrograph of embedded spherical gold nanoparticles in an undulated nanotriangle superstructure.

**Acknowledgements** The financial support of the German Research Foundation (KO 1387/14-1; INST 336/64-1) is gratefully acknowledged.

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# Surface forces and friction mediated by self-assembled polymer spheres, worms, and hollow spheres

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Interfacial polymer layers can be carefully orchestrated through chemical synthesis and self-assembly, leading to controlled geometries and sophisticated structural hierarchy, readily tailoring interfacial properties and inter-surface forces.

Using a surface force apparatus (SFA), we have measured interactions mediated by positively charged polymer nanoassemblies of different geometries and dimensions, including small and large spherical polymer micelles (~30 and 200 nm in diameter respectively), cylindrical polymer micelles (~25 nm in diameter and 200 nm in length), and polymersomes (hollow spheres ~200 nm in diameter), self-assembled from (poly(glycerol monomethacrylate) + quaternized poly(2-(dimethylamino)ethyl methacrylate))-poly(2-hydroxypropyl methacrylate). We find that the polymer worms formed a surface layer with the polymer assemblies partially protruding into the solution, giving rise to a long range repulsion. Our results show that the hollow polymer spheres (polymersomes) adsorbed weakly on the surface, and were expelled out the confining surfaces. Remarkably, the charged polymer spheres remained adsorbed on the surface, displaying stupendous structural integrity and sustaining pressures comparable to those under physiological conditions, mediating extremely effective lubrication, with a friction coefficient  $< \sim 10^{-4}$ .

These unprecedented results facilitate a discussion on the correlation between the geometry and surface charge density of the polymer assemblies, their surface adsorption and interfacial conformation, and the surface forces and friction they mediate.

# Adjusting the Size of Multicompartmental Containers Made of Anionic Liposomes and Polycations by Introducing Branching and PEO Moieties

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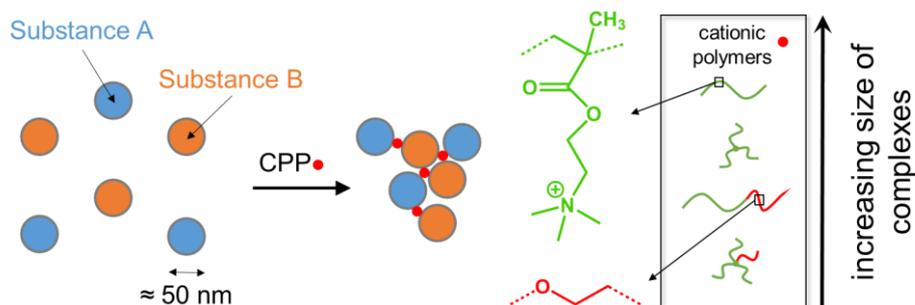
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Multiliposomal containers made of lipid bilayer vesicles (liposomes) could improve the capacity of loading and the release. Such multicompartmental constructs result from the complexation between anionic liposomes with cationic polymers (here quaternized poly(dimethylaminoethyl methacrylate), qPDMAEMA) due to electrostatic attraction [1]. The size of the complexes (investigated by dynamic light scattering) can be adjusted by using a variation of qPDMAEMA samples with similar molecular weight, changing the polymer composition and architecture. We demonstrate the effect of introducing poly(ethylene oxide) (PEO) moieties and/or branching on the size of the hierarchical assemblies: PEO block (present in the miktoarm star-shaped polymer and in the linear diblock polymer) and the branching (of both star-shaped polymers) lead to smaller complexes than the linear homopolymer. These structures of the multicontainers were observed by cryogenic transmission electron microscopy (cryo-TEM). The possibility to load different substances in a multicontainer carrier was verified by two-color fluorescence cross-correlation spectroscopy (FCCS).



**Figure 1** Scheme of the complexation between anionic liposomes and cationic polymers.

**Acknowledgements** This work was supported by the Russian Science Foundation (project 14-13-00255) and the German Research Foundation (Deutsche Forschungsgemeinschaft DFG, project RI 560/22-1).

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# Condensation and Demixing in solutions of DNA Nanostars and their Mixtures

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The pivotal role played by DNA in biology cannot be understated. Its outstanding pairing specificity, embodied by the famous Watson-Crick mechanism, is at the core of its biological functionality. Exploiting such a specificity in synthetic applications, an idea which dates back to the seminal work of Ned Seeman in the 1980's, provides researchers from many different fields, ranging from nanotechnology to material science, with a new, powerful tool [1].

DNA can be used in colloidal systems as a coating agent, but also on its own to self-assemble all-DNA materials with controllable properties. In particular, short DNA strands with carefully designed sequences can self-assemble into well-defined constructs at intermediate temperature. These DNA constructs (nanostars) can, in turn, bind to each other in a controlled fashion to form higher-order structures. Recent experiments have demonstrated that DNA nanostars can be employed as experimental realisations of patchy particles [2, 3], which have shown promising properties as theoretical and numerical model systems for the synthesis of new soft materials such as empty liquids, reentrant gels and open crystals.

Here we present a novel mixed numerical/theoretical approach to efficiently evaluate the phase diagram of these objects. Combining input information based on a realistic coarse-grained DNA potential with the Wertheim association theory we derive a parameter-free thermodynamic description of these systems. We apply this method to investigate the phase behaviour of single-component and mixtures of DNA nanostars with different number of sticky arms, elucidating the role of the system functionality and of salt concentration. The predicted critical parameters compare very well with existing experimental results for the available compositions [4]. Our approach takes into account DNA-DNA interactions in a realistic fashion and therefore is very general and can be easily extended, e.g. to investigate the behaviour of all-DNA systems that incorporates DNA nanotechnology motifs such as hairpins and strand displacements.

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# Bacterial Proteins in real-time: An Atomic Force Microscopy and Quartz Crystal Microbalance with Dissipation study

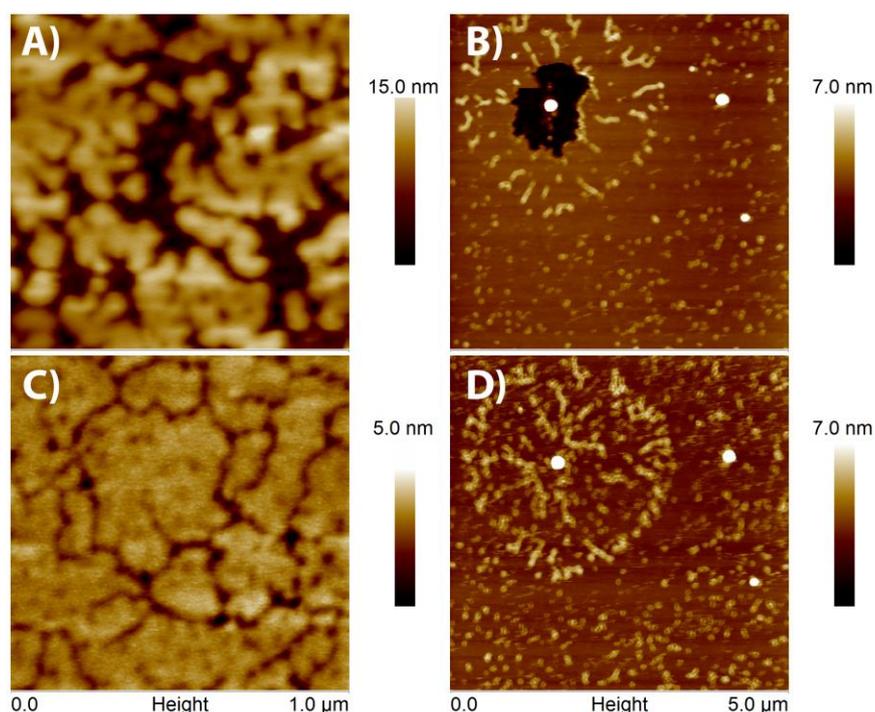
Alberto Moreno-Cencerrado<sup>1\*</sup>, Violetta Golebiewska<sup>1</sup>, Sudarat Tharad<sup>1</sup>, Jagoba Iturri<sup>1</sup> and José Luis Toca-Herrera<sup>1</sup>

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Cytolytic proteins are toxins with the ability of destroying cell membranes, while, on the contrary, surface layer proteins (S-layer) are a fundamental component of the cell envelope in archaea and bacteria. In this talk, we will show the behaviour of the cytolytic Cyt2Aa2 (from *Bacillus Thuringiensis*) and the S-layer protein SbpA (from *Lysinibacillusphaericus CCM2177*) at different interfaces as function of the interaction time and protein concentration.

The combination of Atomic Force Microscopy (AFM) and Quartz Crystal Microbalance with Dissipation (QCM-D) allows us to investigate both systems in real-time in liquid environments [1, 2]. On one hand, we present the ability of SbpA proteins to create 2D crystalline layers. Crystal formation kinetics and surfaces properties such wettability, roughness, viscoelasticity and lattice parameters are the key-factors for the understanding and characterization of this 2D crystal array. On another hand, we will show how cytolytic proteins interact with lipid-cholesterol membranes. The results are discussed in the frame of two “accepted” models: pore-forming like, or detergent like.



**Figure 1** AFM tapping mode micrographs showing protein adsorption and diffusion as a function of time: A)-B) S-layer protein crystal growth within 30 minutes. C)-D) Evolution of the toxin–lipid/cholesterol system within 25 minutes.

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# Colloidal nature of soil organic matter and its interaction with minerals: soil carbon sequestration

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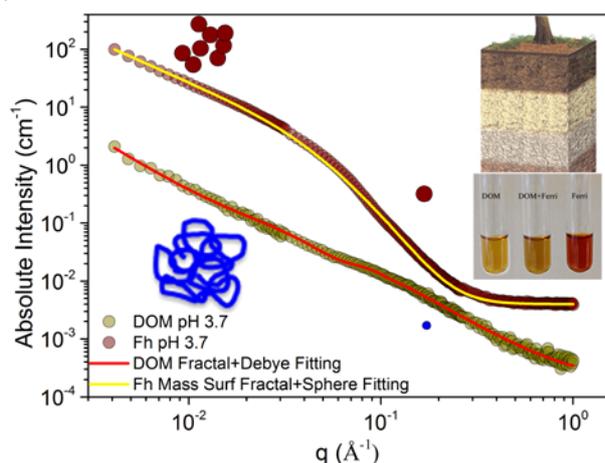
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Organic matter serves as a reservoir of nutrients in the soil, aids in reducing compaction and surface crusting, and increases water infiltration into the soil [1]. The emerging view of soil organic matter (SOM), the largest reservoir of carbon (C) in terrestrial ecosystems, is that stability towards microbial decomposition is controlled by the biological and physicochemical environments and not by SOM chemical composition alone. The molecules co-assemble into supramolecular aggregates that are stabilized by hydrophobic interactions and/or by interactions with mineral particles [2]. The colloidal nature of SOM is hypothesized to influence the extent and kinetics of degradation, and studying the structure of these aggregates, at various stages of SOM degradation, is therefore of great interest.

Small angle X-ray scattering (SAXS) and dynamic light scattering (DLS) were used to characterize colloidal dissolved organic matter, DOM (extract filtered through 200 nm filter), aggregates and their interactions with ferrihydrite ( $\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ ) nanoparticles, a common soil mineral. Figure 1 shows SAXS profiles from extracted DOM and from synthesized ferrihydrite particles, respectively. The data indicate the presence of at least two different kind of DOM aggregates. Ferrihydrite (Fh) is a widespread hydrous ferric oxide mineral at the Earth's surface. In our studies, we used Fh synthesized in the lab obtaining particles ("six-line") with an average particle size below 10 nm [5], however these particles may aggregate onto clusters, depending on pH. In the pH range 3-8, Fh mineral particles have a positive charge, while DOM has a net negative charge, and are therefore expected to co-assemble. Systematic SAXS and DLS investigations were performed on DOM-Fh systems to understand the mechanism of interaction and colloidal their properties.



**Figure 1:** SAXS profile of dissolved organic matter (DOM) extracted from litter was fitted by a model (red solid line) combining large fractal aggregates [3] and smaller oligomeric species described by the Debye model [4], having an average radius of gyration of ca. 20 Å. However, the colloidal structure (e.g. the fractal dimension) may differ between different soil extracts, which is something to take into account when working with natural materials. The SAXS profile of synthesized ferrihydrite (Fh) was fitted by a model (yellow line) combining the mass surface fractal (>200 nm) and sphere (5 nm).

**Acknowledgements** This work was supported by Knut and Alice Wallenberg Foundation. LG acknowledge support from Landshövding Per Westlings Minnesfond (Lund University).

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# Water-in-Water (w/w) emulsions for preparing microgels

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Water-in-water (W/W) emulsions are liquid/liquid dispersions of two immiscible aqueous phases, in absence of both oil and surfactant. These colloidal dispersions can be prepared in aqueous mixtures of two hydrophilic polymers, in which segregative phase separation occurs because of mutual incompatibility between the two polymers [1,2]. The present work focuses on the study of emulsion droplets in H<sub>2</sub>O/protein/polysaccharide systems. Fig. 1 shows examples of gelatin-in-maltodextrin and maltodextrin-in-gelatin W/W emulsions.

Different methods of emulsion formation have been studied, and the results have demonstrated that small droplets can be obtained by fast nucleation, inducing a phase transition from a single-phase region to a two-phase region of the phase diagram.

Microgel particles can be obtained by dispersing a gelatin aqueous solution into a maltodextrin aqueous solution at 50°C, and then cooling down to 25°C. The stability of such microgels has been greatly improved by crosslinking with genipin. The encapsulation of active components inside these microgel particles has also been studied.

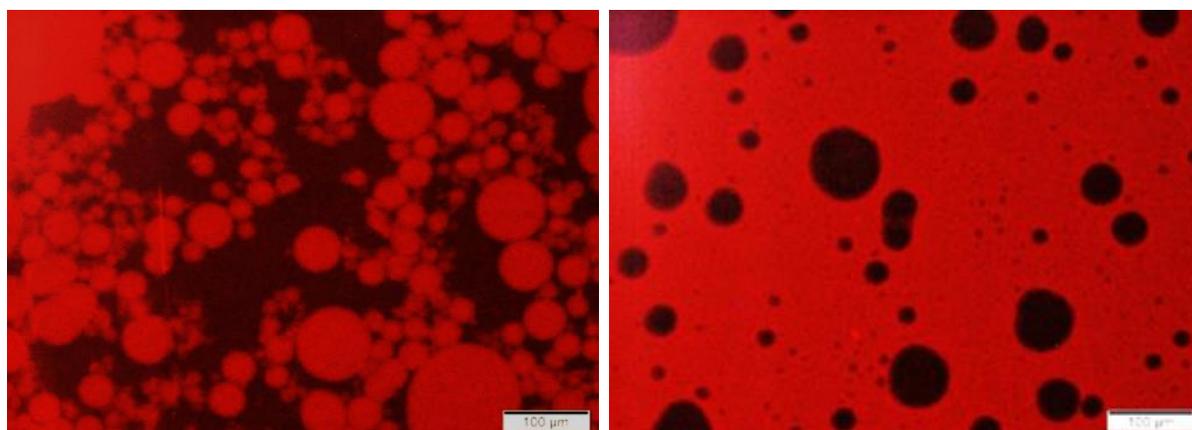


Fig. 1. Optical microscopy image of a gelatin-in-maltodextrin emulsion (left) and maltodextrin-in-gelatin emulsion (right), both observed by fluorescence optical microscopy using labeled gelatin.

## Acknowledgements

People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n°606713 (BIBAFODS project).

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# Structural Characterization of Hollow Doubly Thermoresponsive Microgels

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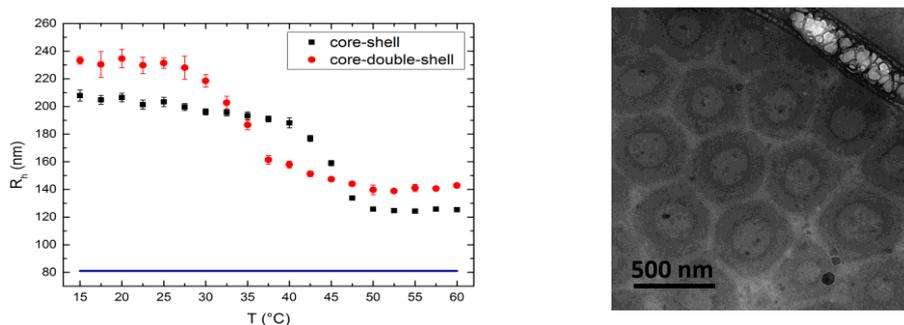
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Hollow doubly thermoresponsive microgels reveal promising properties for applications as novel carrier systems [1]. Such hollow structures can be obtained from the synthesis of a sacrificial surface modified silica core with two spatially separated polymeric shells. Subsequent core dissolution leads to the generation of the corresponding hollow double-shell microgels [2]. The use of two different polymers forming the shells ensures distinct volume phase transition temperatures (VPTTs) of both networks leading to an advanced thermoresponsiveness. This enables a separate control of the interactions between both the microgel and its surrounding and the microgel and possible guest species inside the cavity. Here, we present core-double-shell microgels and the corresponding hollow capsules made of an inner poly(*N*-isopropylmethacrylamide) (pNIPMAM) and an outer poly(*N*-isopropylacrylamide) (pNIPAM) shell. The VPTTs of 44 °C for pNIPMAM and 34 °C for pNIPAM lead to a doubly thermosensitivity. The shell thicknesses and permeabilities are of great importance regarding the stability and structure of the hollow microgels. The temperature triggered changes in size and structure have been investigated by dynamic light scattering (Fig. 1 *left*) and small-angle neutron scattering showing a strong interplay of the shells. Especially interesting effects on the relative polymer volume fraction as well as the cavity of the microgels were observed at temperatures between the distinct VPTTs. We observed a strong interpenetration of the shells in the presence of the stiff silica core. The corresponding hollow spheres show conservation of the cavity at all swelling degrees (Fig. 1 *right*) and provide required properties for a controlled uptake, storage and release of guests.



**Figure 1** *Left*: Thermoresponsiveness of silica-core pNIPMAM-shell and silica-core pNIPMAM-shell pNIPAM-shell microgels. *Right*: Cryo-TEM image of the corresponding hollow double-shell microgels.

**Acknowledgements** The authors acknowledge funding from the Deutsche Forschungsgemeinschaft for financial support within SFB 985 “Functional microgels and microgel systems”.

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# Plastic restructuring and intermittent dynamics in a thermoreversible colloidal gel

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Physical gels, held together by attractive interparticle forces comparable to the thermal energy, undergo restructuring processes characterized by a highly nonlinear dynamics, which last for extremely long time driving a progressive structural ageing [1,2].

We have synthesized an aqueous colloidal system where interparticle interactions can be accurately tuned by exploiting the temperature dependence of the affinity with the solvent of a suitably designed stabilizing layer. In addition, the particles are closely matched in refractive index with water, which allows space-resolved optical correlation techniques such as Photon Correlation Imaging to be used [1,3].

By increasing the temperature, the suspension is driven into a miscibility gap, where reversible gels form. Similarly to what we previously found for depletion gels, these arrested structures undergo a first compressional stage, driven by the gravitational stress, in which the microscopic dynamics is fully ruled by the macroscopic strain [1,3]. At the end of this compression stage, the gel is subjected to sudden “restructuring bursts”, due to the release of frozen local stresses, leading to a momentary partial fluidization the system, which repetitively occur during the gel ageing. A very peculiar effect, not previously evidenced for any colloidal or biopolymer gel [1,2,3,4], is that each one of these plastic restructuring events leads, once the gel has recovered its arrested state, to a drastic slow-down of the microscopic dynamics. Besides, an overall fluidization event is usually anticipated by a series of microscopic rearrangements, which are clearly evidenced by a spatially—resolved activity map. Finally, the repletion in time of the major restructuring events display a distinctive scaling behaviour with the gel ageing time.

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# Antibacterial LbL coatings to control drug release from ophthalmic lens

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The use of contact lenses to correct vision problems together with the substitution of natural lenses by intraocular lenses in cataract surgery have improved the quality of life of millions of patients. However, the surface of these devices is also prone to microbial pathogens adhesion which has a central role in causing infections [1]. A possible strategy to overcome these undesirable effects could be by modifying the lens material or using coatings to prevent adherence and colonization [2].

One efficient way to reduce bacterial cell adhesion is to coat the surface of the ophthalmic lenses using the layer-by-layer (LbL) technique. In a recent review, Guo et al [3] described the use of LBL coatings to control cell adhesion to biomaterials surfaces.

In this study we investigated the possibility of using polyelectrolytes with anti-bacterial properties to form layer-by-layer (LbL) coatings on contact lens materials with the objective of controlling the release of ophthalmic drugs, while keeping minimal bacterial cell adhesion on the lens surface. A silicone-based hydrogel recently proposed by our group was chosen as drug releasing soft contact lens (SCL) material and three drugs were tested: moxifloxacin, chlorhexidine, and diclofenac. The most promising coatings involved combinations of alginate (ALG), chitosan (CHI), hyaluronate (HA) and polylysine (PLL), using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) as a cross-linking agent. The coatings consisting in one double layer of ALG/PLL/EDC, HA/EDC/CHI and HA/PLL+EDC+Drug proved to have excellent features to control the release of diclofenac, while keeping or improving the biological and physical properties of the lenses. A top layer of HA is needed to reduce the interaction with tear protein. However, the barrier effect of these coatings is specific for diclofenac, giving evidence to the importance of the formation of reversible bonding between the carboxyl groups of diclofenac and the amine groups of PLL or CHI through the activating action of EDC to sustain the drug release.

**Acknowledgements** The authors thank Fundação para a Ciência e a Tecnologia for Diana Silva PhD Grant (PD/BD/114088/2015), and for funding through the project PTDC/CTM-BIO/3640/2014. Dr Clara Gomes from CQE-IST is greatly acknowledged for providing polystyrene.

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# Weak polyelectrolyte microgels in a non-aqueous polar solvent

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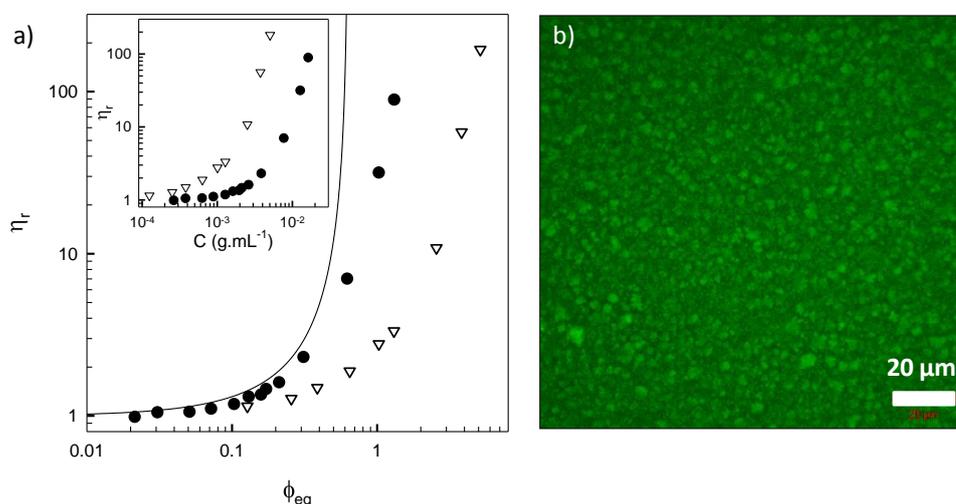
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The carbomer microgels are highly crosslinked hydrophilic nanoparticles based on polyacrylic acid (PAA), used in aqueous solution as a gelling agent in many products of everyday life [1]. The objective of this work is to investigate their gelling potential in a non-aqueous and green solvent, glycerol, and to understand the effects of different factors, such as the ionization state ( $\alpha$ ) of the AA units. For this, we have implemented a bottom-up physical-chemical approach, using rheology and structural characterization techniques to establish the structure-property relationship in carbomer glycerol “gels”.

The liquid/solid transition observed for this system, quantified by rheology, can be interpreted in a similar way to that in a colloidal suspension [2]. The microgels form colloidal gels above a critical glass transition ( $C_G$ ) concentration by volume filling. The ionization of these PAA based microgels, in the non-aqueous but moderately polar glycerol, makes it possible to shift this glass transition to a lower concentration (see Figure 1a insert), in a manner comparable to its pH responsive behaviour in water. This is attributed to the microgel swelling induced by the repulsion between the ionized AA units. Consequently, the deformability of the microgels increases, resulting in a “softer” glass transition [3] than in the case of hard spheres suspension (see Figure 1a). In addition, the observation by confocal microscopy of this system in glycerol shows that the microgels have an irregular structure with an average characteristic size of  $\sim 5 \mu\text{m}$ . Moreover, these microgels are not aggregated (see Figure 1b), which confirms the repulsive interactions between the microgels.



**Figure 1** a) Relative viscosity as a function of effective volume fraction for neutral ( $\alpha = 0$ ,  $\bullet$ ) and ionised ( $\alpha = 1$ ,  $\blacktriangledown$ ) carbomer microgels solutions in glycerol. The solid line represents a hard sphere model. Insert: Same data before concentration axis rescaling. b) Confocal microscopy image of a carbomer microgels solutions in glycerol at 1 wt%.

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# New Biofuel Formulations

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Due to increasing environmental problems caused by the consumption of fossil fuels, biofuels are currently in the focus of intensive research. Vegetable oils are the most available source of biomass that could be used as biofuels. However, their high viscosities and melting points cause many problems that make a direct usage in engines very difficult. Therefore, they are further processed to fatty acid methyl esters by a transesterification reaction with methanol. Nevertheless, these low viscous liquids, that are usually called biodiesel, still possess high melting points and the processing is time-consuming and leads to several by-products.

We successfully formulated biofuels that solve the abovementioned problems concerning the usage of vegetable oils (patent pending). For that, detailed investigations on the miscibility of all components were necessary. In collaboration with the engineering department of our neighbouring technical university of applied sciences, several engine tests were additionally performed to get to the optimal fuel formulation. Eventually, we obtained a new class of biofuels, whose compositions can be adapted depending on the application. Various physicochemical problems that occur due to the usage of vegetable oils could be solved. Further, the difficulties concerning the miscibility of the components could be fixed without using any surfactants. The engine tests of the final formulations consisted of ignition delay, emission and consumption measurements as well as investigations on their combustion processes. It could be shown that the formulated biofuels are very close to diesel concerning their ignition delay properties. Surprisingly, the gaseous as well as soot emissions are comparable to or even lower than those of diesel. Especially at higher boost pressures, the formulated biofuels show distinctly less emissions than diesel. Even if the biofuels lead to slightly higher consumptions, their costs are lower than the current diesel price, which compensates this drawback. The already mentioned comparability to diesel can also be observed by the combustion processes, which are very similar. With these new biofuel formulations, an important step towards completely sustainable biofuels was achieved including the applicability of vegetable oils without further drawbacks.

# Hardening of particle/water/oil three-phase dispersions due to capillary bridges with applications for new products and materials

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Theodor D. Gurkov<sup>1</sup>, Simeon D. Stoyanov<sup>2</sup>, Eddie G. Pelan<sup>2</sup>

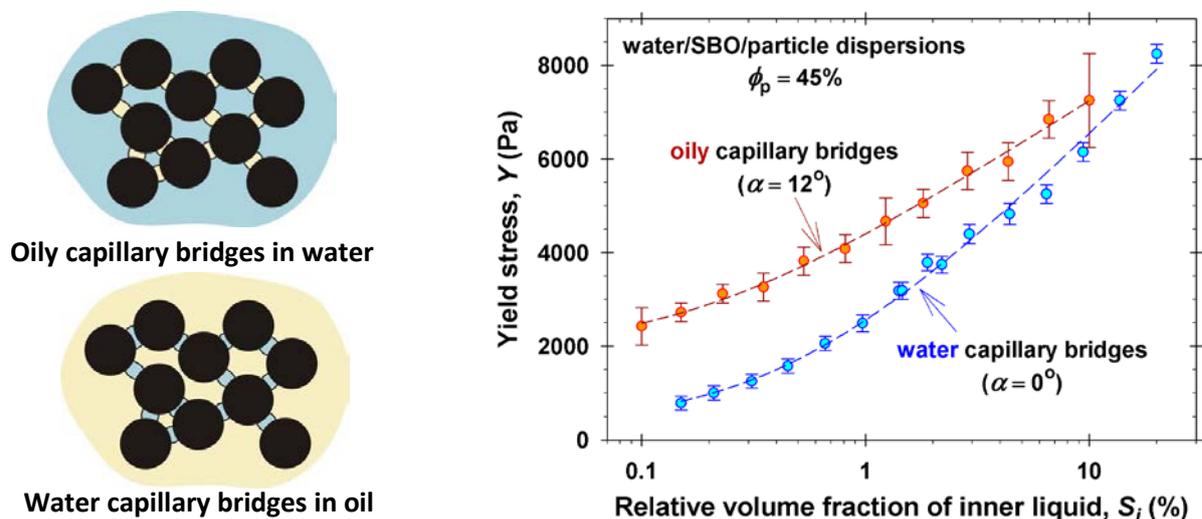
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The subject of this study is the rheological behavior of three-phase dispersions particles/water/oil. In this area, there is a vast unexplored concentration gap between the phase domain of particle networks (particle volume fractions  $\phi_p < 30\%$ ) [1] and the domain of wet granular materials ( $\phi_p > 70\%$ ) [2]. The objective of our studies is to experimentally investigate and theoretically interpret the rheological properties of dispersions in the intermediate region,  $30\% < \phi_p < 70\%$ . They possess the remarkable property that the addition of a minimal amount of the second (disperse) liquid phase leads to strong solidification of the dispersion owing to the interconnection of the particles by capillary bridges. The yield stress,  $Y$ , of the dispersions is investigated for various  $\phi_p$  values. Quantitative theoretical model is developed, which relates  $Y$  with the maximum of the resultant of capillary bridge force as a function of shearing angle. The model agrees very well with the experimental data. For water-in-oil bridges,  $Y$  is systematically lower than for the respective oil-in-water bridges (Figure 1) because of electrostatic repulsion between the particles across the oil phase [3], which opposes the capillary-bridge attraction.

The results could have importance for various materials in chemical and food industries, construction materials and cosmetics, which represent solid/water/oil three-phase dispersions.



**Figure 1.** Oily vs. water capillary bridges: comparison of the measured yield stress; SBO = soybean oil.

**Acknowledgements:** The financial support of Unilever and of the Horizon 2020 project ID: 692146-H2020-eu.4.b "Materials Networking" is gratefully acknowledged.

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# Distance-dependent structures of interacting membranes displaying synthetic polymers and wild-type bacterial lipopolysaccharides

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Polymer brushes are found on the surfaces of important classes of biological membranes, such as lipopolysaccharides (LPS) on bacterial outer membranes [1]. The latter mediate the interaction with other bacteria and thus influence the physical properties of bacterial biofilms[2]. But interacting polymer brushes are also of technological relevance, for instance in the field of surface lubrication[3]. The interaction between polymer-decorated surfaces is coupled to the distance-dependent conformation of the polymer chains. This problem has been addressed by theory[4-7], but accurate experimental data on polymer conformations under confinement are rare[8, 9].

Here, we utilize neutron reflectometry (NR) to determine the distance-dependent structure of interacting lipid membrane surfaces decorated with hydrophilic poly(ethylene glycol) (PEG) brushes. To gain insight into bacterial interactions in biofilms we also investigate the structure of two interacting surfaces formed by wild-type bacterial lipopolysaccharides with strain-specific O-side chains.

For the first time, we achieve structural insight into wild type LPS from Gram-negative bacteria. The effect of divalent cations removal (*e.g.*  $\text{Ca}^{2+}$ ) is also studied. The results highlight the importance of salt bridges formed by divalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  with negatively charged sugars in LPS core oligosaccharide. These interactions appear to be crucial to the structural integrity of the outer membrane, with the disruptive nature of the electrostatic repulsive forces between adjacent LPS molecules revealed when charge screening is removed.

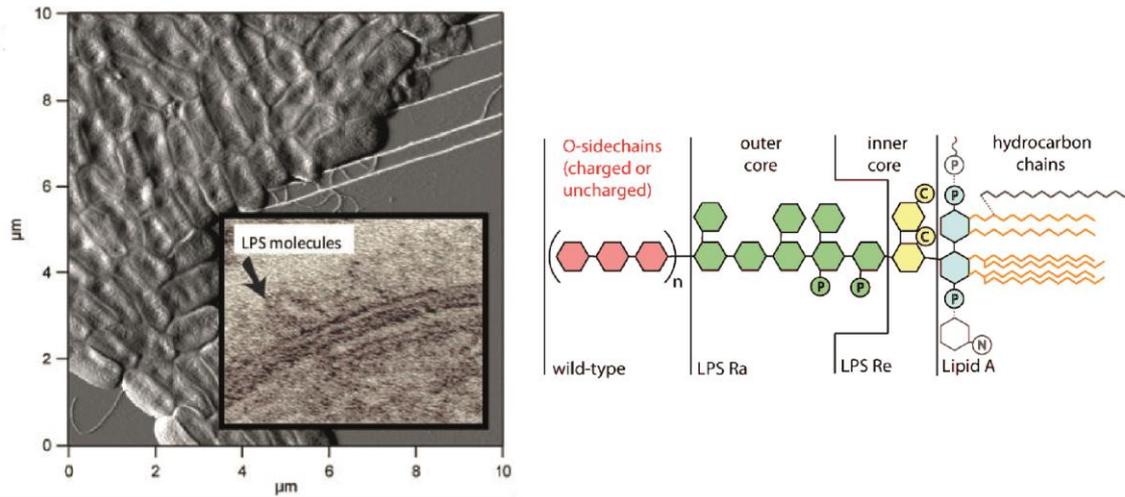


Figure 1: (Left) Bacterial biofilm. The inset shows the bacterial outer membrane. (Right) Schematic representation of a LPS molecule.

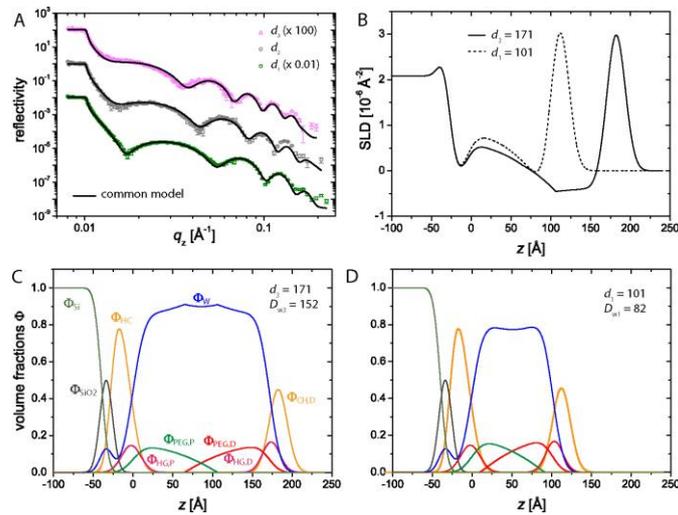


Figure 2: Results for two interacting PEG-decorated lipid membranes at different surface separations,  $d$ . A) Neutron reflectivity. B) SLD profiles. C) and D) Volume fraction distributions.

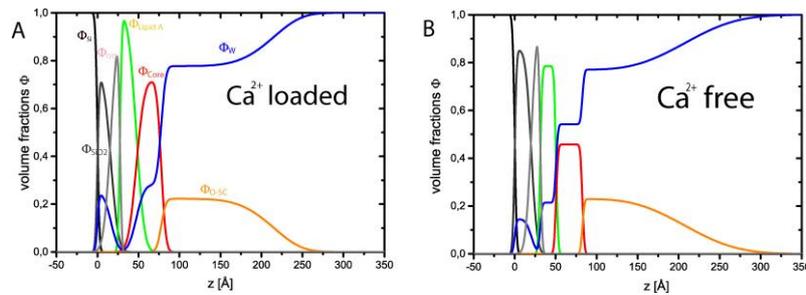


Figure 3: Single LPS surface before (A) and after (B) Ca<sup>2+</sup> removal. Volume fraction distributions obtained from NR data analysis.

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# Shrinking Armored Droplets to Advance New Materials for Applications

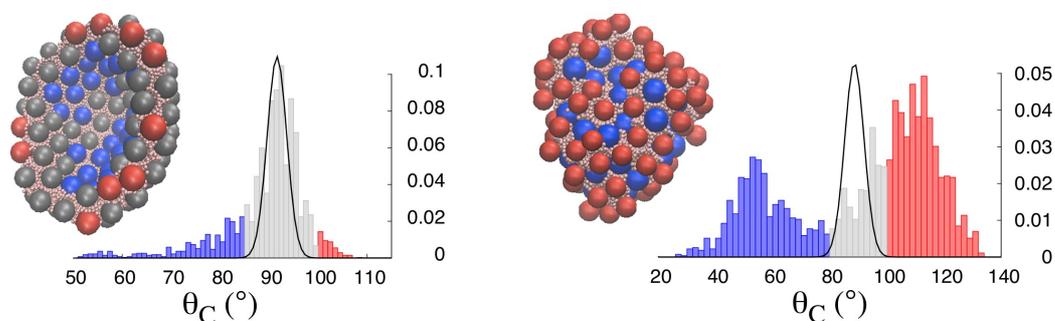
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Pickering emulsions, *i.e.* particle-stabilized emulsions, have been studied intensively in recent years owing to their wide range of applications including biofuel processing and food preservation. They have also been developed as precursors to magnetic particles for imaging and drug delivery systems. In some important processes that involve emulsions, it can be required to reduce the volume of the dispersed droplets. The interface may undergo large deformations that produce compressive stresses, causing localized mechanical instabilities. The proliferation of these localized instabilities may then result in a variety of collapse mechanisms. Numerous experiments have been conducted to link the rheological response of particle-laden interfaces to the stability of emulsions and foams. However, due to their inherent limited resolution, direct access to local observables, such as the particles three-phase contact angle distribution,  $\theta_C$ , remains out of reach. This crucial information can be accessed by numerical simulations, sometimes with approximations. All-atom molecular dynamics (MD) simulations have then become a widely employed computational technique. However, they remain computationally expensive. Mesoscopic simulations, in which the structural unit is a coarse-grained representation of a large number of molecules, allow us to overcome this limitation.

In this talk, the issue of the buckling mechanism in droplets stabilized by solid particles (armored droplets) is tackled at a mesoscopic level using Dissipative Particle Dynamics (DPD) simulations. We consider spherical water droplet in a decane solvent coated with nanoparticle monolayers of two different types: Janus and homogeneous. The chosen particles yield comparable initial three-phase contact angles, chosen to maximize the adsorption energy at the interface. We study the interplay between the evolution of droplet shape, layering of the particles, and their distribution at the interface when the volume of the droplets is reduced. We show that Janus particles affect strongly the shape of the droplet with the formation of a crater-like depression (cf. Fig.1, left panel). This evolution is *actively* controlled by a close-packed particle monolayer at the curved interface. On the contrary, homogeneous particles follow *passively* the volume reduction of the droplet, whose shape does not deviate too much from spherical, even when a nanoparticle monolayer/bilayer transition is detected at the interface (cf. Fig.1, right panel). We discuss how these buckled armored droplets might be of relevance in various applications including potential drug delivery systems and biomimetic design of functional surfaces.



**Figure 1** Three-phase contact angle distribution of Janus (left panel) and homogeneous (right panel) nanoparticles at the initial stage (continuous black lines) where the shape of the droplet is spherical, and at the final stage (histograms). The droplet configurations at the final stage are also shown. The blue, gray, and red spheres represent the nanoparticles with contact angles in the three respective regions highlighted in the histogram distributions.

# Radiolysis of gold ions trapped within charged copolymer at the air/water interface: a promising route for the fine tuning of gold nanoparticles synthesis

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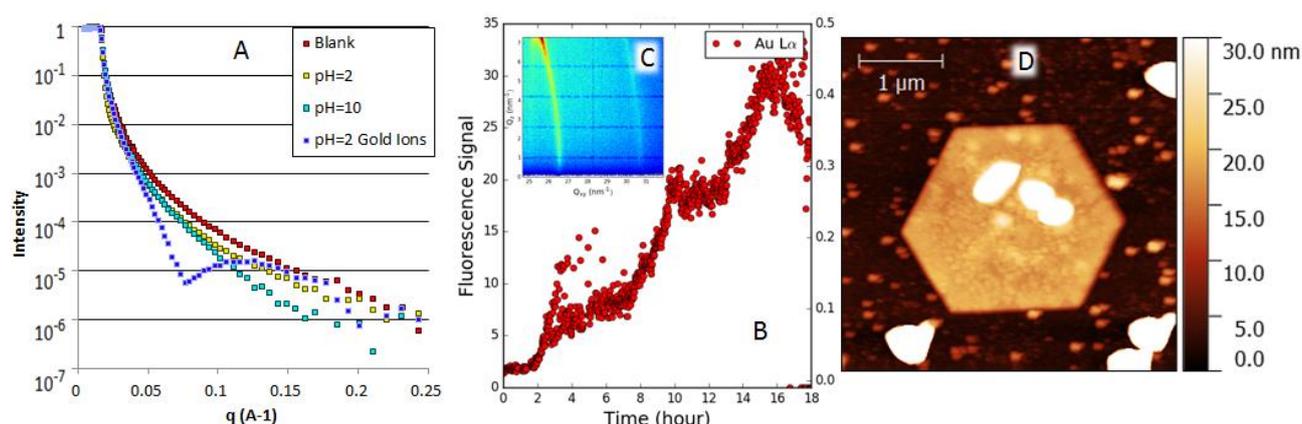
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Controlling size and spatial distribution of gold nanoparticles is an expanding field of research of nanoscale science with multiple potential applications [1]. For such purposes, we are developing surface radiolysis at the air/water interface by irradiating with x-ray at grazing incidence a charged organic monolayer template interacting with metal ions in the subphase [2]. Using block copolymers such as PS-*b*-PDMAEMA to obtain a larger variety of surface templates is a promising route. The PDMAEMA block is an aminated monomer, positively charged at acidic pH and neutral otherwise. Deposited on the water surface, the hydrophobic polystyrene block anchors the copolymer at the interface, the hydrophilic PDMAEMA block being free to self-organize under the surface. The structure formed depends strongly on pH, ionic strength and molecular area allowing tunable structures. Moreover the positively charged copolymer is expected to interact with negative ions such as AuCl<sub>4</sub><sup>-</sup> in the subphase.

Those systems have been first studied by neutron reflectivity allowing for a selective matching of each of the copolymer blocks. The copolymer forms thick layer whose structure depends on pH while the copolymer/gold ions system forms a thinner, denser and very rigid layer constrained near the interface (FigA). This indicates a trapping of gold ions within the PDMAEMA brush. Radiolysis induced reduction of gold ions was then done by x-ray irradiation of the rigid copolymer/gold ions layer while measuring simultaneously GIXD and surface fluorescence on the SIRIUS beamline at SOLEIL synchrotron. A steady increase of the gold concentration measured by fluorescence is observed during the radiolysis (FigB) and gold crystals diffraction peaks are observed (FigC). Atomic Force Microscopy of the retrieved post-radiolysis layer displays gold nanoparticles with a striking hexagonal shape (FigD).



**Figure 1:** (A) Neutron reflectivity of the PDMAEMA block monolayer at pH=2 (yellow) and pH=10 (cyan) and pH=2 + Gold Ions at 10<sup>-5</sup> M (blue) (B) Surface fluorescence of Au during the radiolysis process (C) GIXD spectrum at the end of radiolysis (D) AFM of a gold nanoplate formed (thickness = 16 nm)

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# Fluorescent carbon-based multivalent nanoplatforms for glycan presentation

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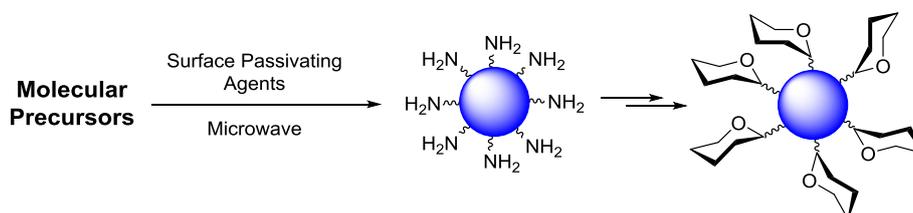
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Carbohydrates expressed on cellular surfaces are presented in a multivalent fashion. This “cluster-glycoside effect” is used by Nature to compensate for weak-binding events between single saccharides and carbohydrate-binding proteins i.e. lectins.<sup>1</sup> Platforms that recreate this multivalent presentation represent a good biomimic of the cell surface, our group recently showed that the type of glycan presented on the surface of a fluorescent CdSe/ZnS quantum dots (QDs) had an effect on intracellular uptake, furthermore a QD coated with lactose and a non-internalisable sugar were up-taken into HeLa and human corneal epithelial cells (Araki-Sasaki).<sup>2</sup> Although we showed that glycan density mitigates the inherent toxicity of CdSe QDs, these nanodots remain less than ideal for *in vivo* applications. In order to broaden the scope of functional nanomaterials for biomedical applications, it is of the utmost importance to develop non-toxic and stable nanomaterials that can be used over long periods of exposure.<sup>3</sup>

Carbon-based fluorescent nanomaterials have shown great potential as an alternative. Carbon dots (CDs) are a relatively recent discovery that have QD-analogous photoluminescence properties e.g. tuneable fluorescence, but crucially are also highly water soluble, easily functionalized and have benign toxicity profiles.<sup>4</sup> Herein, we report the facile and fast synthesis (three minutes) of a new class of fluorescent CDs using microwave-assisted irradiation from simple and cheap molecular precursors, in the presence of surface passivating agents.<sup>5</sup> Novel features, not previously described in other CDs were identified including a sp<sup>3</sup>-nanocrystalline core and important incorporation of chlorine into the CD architecture, which contributed to quantum yield. Subsequent surface manipulations on the CD can afford glycan-coated CDs (Figure 1) which have been investigated for their cellular uptake, toxicity profile and their potential use as carbohydrate multivalent platforms. Plus, small reaction modifications allow interesting features to be integrated into the system such as tuned fluorescence and sub-cellular localisation.



**Figure 1:** Synthetic outline for carbohydrate-coated carbon dots

**Acknowledgements** The financial support of the Bristol Chemical Synthesis CDT and EPSRC.

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# Luminescence-based Nanothermometers to Control Plasmonic Heaters

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Temperature is a key parameter for life, since it can only happen and prosper in a very narrow thermal range. Accordingly, nanoheaters that can be remotely activated have been proposed to conduct thermal therapy (to kill infectious or tumorous agents by increasing temperature) inside the human body. The most spread type of heaters at the moment are based on magnetic materials. However, light-triggered heating is becoming a relevant alternative option [1, 2]. In this work, we compare different plasmonic nanoparticles from the point of view of their heating ability and their stability. All the different structures analyzed have been chosen to be excited in the near-infrared range, since this allows for higher penetration depth than visible light, which is to a larger extent absorbed by biological tissues.

Regardless the heater, in order to optimize the efficiency of the therapy and to minimize the chances of overdose that could damage the surrounding healthy area, it is important to develop strategies to control *in situ* the reached temperature [3]. With this idea in mind, we are synthesizing Nd<sup>3+</sup>-based nanoparticles. These particles can be excited at the same wavelength used to activate the heaters, and thus, the combination of both constitutes a heater/thermometer pair fully working within the biological windows.

**Acknowledgements** This work is funded by the European Union (Horizon 2020) through a Marie Skłodowska-Curie Action awarded to Marta Quintanilla (PHELLINI).

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# Improved Performance of Magnetic Colloids for Heat Delivery and Magnetic Guidance Applications

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Nanoparticles of magnetic materials are very useful in different bio-related applications, on which the combination of chemistry and magnetic performance will determine their final purpose. Two examples of magnetic nanoparticles synthesized and manipulated by wet-chemistry methods will be detailed to demonstrate how to exert control over the final magnetic behavior and over their ultimate functionalities, considering heat delivery or magnetic guidance of self-propelled swimmers.

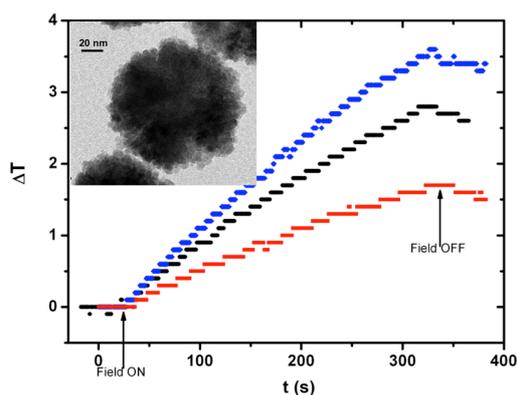


Figure 1. Temperature kinetics of aqueous dispersions of colloidal clusters of manganese ferrite nanoparticles during the application of an alternating magnetic field.

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# Nanoparticles from Step-Growth Radical Thiol-Ene Emulsion Polymerizations

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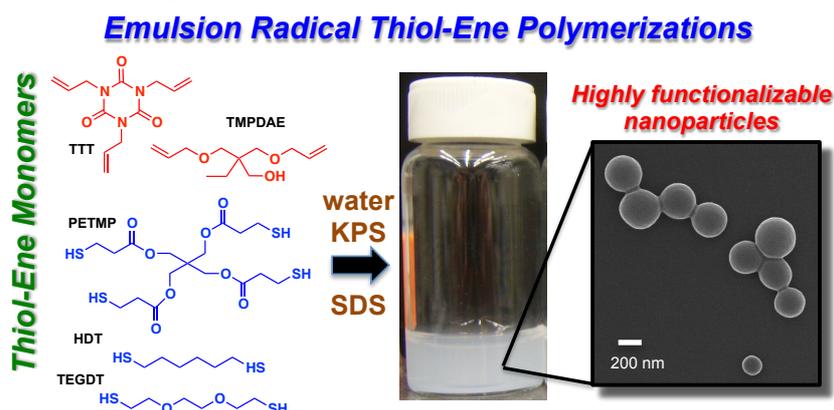
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Recent developments in radical-mediated thiol-ene polymerizations include the application of these polymerizations in emulsion, dispersion, and suspension polymerizations [1-6]. These step-growth polymerizations have several significant advantages over traditional chain-growth (e.g., acrylic or styrenic) polymerizations. In particular, they allow for easy functionalization through simple stoichiometric adjustments of the monomers used in the polymerization; for example, adding a slight excess of thiol monomer produces colloidal polymer particles replete with thiol functionality. Furthermore, the subsequent use of thiol-ene (and thiol-yne) and other 'click' chemistries can lead to the facile production of biodegradable and bio-functionalized colloids.

Our early publications [1-5] showed that radical thiol-ene polymerizations can easily be performed in suspension, mini-emulsion and dispersion polymerizations. In each of these cases, the initiator is oil (monomer) soluble, and thus particles grow either from the monomer droplets (in the cases of suspension or mini-emulsion systems), or from the precipitation of the growing polymer (in dispersion polymerizations). Very recently, we have shown that by using a water-soluble initiator, such as potassium persulfate (KPS), it is possible to perform thiol-ene polymerizations under conditions that essentially mimic those of traditional vinyl monomer emulsion polymerizations [6]. Furthermore, the formation of nanoparticles that may be uniform in size is possible.

In order to understand how reaction conditions affect particle size and polydispersity in these newly developed thiol-ene emulsion polymerizations, we have conducted a thorough study of these polymerizations using a wide range initiator (KPS) and surfactant (sodium dodecyl sulfate, SDS) concentrations, with several different thiol- and ene-monomers (see Figure 1). Results from this study will be discussed, and conclusions regarding particle nucleation and growth mechanisms will be drawn.



**Figure 1.** Outline of radical-mediated thiol-ene emulsion polymerizations.

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# Dual delivery nanosystem for drugs and biomolecules. Formulation, characterization and in vitro release.

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Due to the biocompatible and biodegradable properties of Polylactide glycolic acid (PLGA), nanoparticles (NPs) based on this polymer have been widely studied for use as drug/biomolecule delivery vehicles for long-term sustained-release preparations [1]. The use of the polymeric surfactant Pluronic F68 in the synthesis procedure has an effect on the reduction of the size of the NPs, the enhancement of their stability and the protection of the encapsulated biomolecule [2]. In addition, the recognition of the nanocarriers by the mononuclear phagocytic system (MPS) is reduced [3]. In this work, two different synthesis methods for Lysozyme-loaded PLGA NPs have been developed and optimized, they both based on the double-emulsion (water/oil/water, W/O/W) solvent evaporation technique [2]. Lysozyme is considered as a model for the bone morphogenetic protein 2 (BMP2)[4]. They mainly differ in the phase the surfactant (Pluronic F68) is added, and in the technique to apply the mechanical energy. Spherical hard NPs are obtained with the two methods. However, in one case, they are monodisperse, with diameters around 120 nm, and in the other case, a polydisperse system of NPs with diameters between 100 and 500 nm is found. The colloidal properties of these systems (morphology by SEM and STEM, hydrodynamic size by DLS and Nanoparticle Tracking Analysis, electrophoretic mobility, temporal stability in different media, protein encapsulation and release) have been analyzed. The interaction surfactant-protein depending on the synthesis procedure has been mimicking by means of an interfacial characterization (surface tension and dilatational rheology). Finally, cellular uptake by bone cells, and cytotoxicity for both systems have been compared. The multimodal system is found to be a promising “dual delivery” system for encapsulating hydrophilic proteins whose biological activity is important at cell surface and cytoplasm level.

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# Flame retardant nanocontainers with variable morphology by polyaddition reaction in inverse miniemulsion

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Since we live in the polymer age, and polymers are highly inflammable, flame retardants have become a key component in industry to reduce the impact of fires. However, traditional flame retardants like halogenated compounds present some serious disadvantages, like environmental persistence and toxicity, and their use is currently limited by REACH (EC 1907/2006). Halogen-free flame retardants like organophosphorus compounds or metal hydroxides, on the other hand, deteriorate the mechanical properties and have poor effectiveness. Thus, over last years, the development of fire-resistant nanomaterials encloses one of the most promising challenges in the area of flame retardancy, considering that they can simultaneously enhance mechanical and thermal properties, accompanied by an excellent barrier performance [1].

Several mostly inorganic materials such as montmorillonite clays, carbon nanotubes, silica particles or metal oxide nanoparticles, have been reported [2]. Nevertheless, they also show considerable damage in the mechanical properties of the polymer matrices, as a result of their poor dispersion and poor interfacial adhesion with them due to their inorganic nature. To overcome these disadvantages, herein, a new approach based on the development of polymeric flame retardant nanocontainers with high thermal stability, low flammability and good compatibility with polymeric matrices is presented.

A novel organophosphinine monomer (6,6'-(bis(4-aminophenyl)methylene)bis(dibenzo[1,2]oxaphosphinine 6-oxide)) with high thermal stability was used as a chemical building block for the generation of polyurea nanocontainers via polyaddition reaction in inverse miniemulsion [3]. A microfluidizer was chosen as a homogenization method to satisfy the demanded scaling of the final application. The performance of the miniemulsion in a dynamic high-pressure system exhibited an unexpected result on the morphology. Nanocontainers (200 nm of diameter) with spherical and cylindrical morphology depending on the process parameters were achieved, affording a new route to various nanoparticle morphologies.

Furthermore, the nanocontainers were introduced into epoxy resins. Several temperatures and mixing times were studied to get a good stabilization and dispersion of the nanocontainers in the epoxy media. The interfacial adhesion between the nanocontainers and the matrix was reduced by the organic nature of the nanocontainers and the functional groups (NH<sub>2</sub> or NCO) on their surface. A low effect of the nanocontainers on the glass transition temperature was observed. The thermal stability was improved with respect to their charring behaviors.

**Acknowledgements:** The authors thank the Marie Skłodowska-Curie fellowship 705054-NOFLAME (Flame Retardant Nanocontainers) project

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# Colloidal stability of clay platelets in the presence of oppositely charged inorganic ions, polyelectrolytes or polymeric particles

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Tuning colloidal stability of clays in aqueous dispersion is essential to design stable systems or to induce controlled aggregation of these particles depending of the potential future application. Therefore, the understanding of the importance of the ionic or polymeric environment effect on the particle aggregation processes is crucial. We aimed at investigating the influence of ionic species from mono through multi to polyvalent ions on the colloidal stability of colloids containing anionic clays.

First, the colloidal behavior of the clay material (layered double hydroxide, LDH) was investigated in the presence of oppositely charged mono, di, tri and tetravalent salts by employing dynamic light scattering (DLS), transmission electron microscopy (TEM) and electrophoretic mobility measurements. Monovalent salts destabilized the particles by screening their charge [1,2]. Second, ions with higher valences, beside screening, exhibited pronounced adsorption, which caused significant overcharging. In case of tetravalent salts and polyelectrolytes even such an overcharging induced the restabilization of the suspensions at intermediate doses in the stability plots. In addition, the critical coagulation values (CCC) dramatically decreased by increasing the valence (Fig 1a) [1]. The polyelectrolyte-induced LDH aggregation was sensitive to the concentration of the polymeric materials. Most importantly, highly stable dispersions, suitable for further applications in preparation of composite materials and carrier particles, can be designed once the appropriate polyelectrolyte loading is applied [2-4]. Moreover, the surface of charged polymeric latexes were functionalized by oppositely charged LDH particles. In case of charge neutralization, the aggregation was faster than the diffusion limited aggregation of the latexes probably due to the formation of LDH patches, which caused so-called patch-charge attractive forces (Fig 1b) [5].

The obtained results give us insight into the colloidal behavior of clays in different environments, shed light on the charging and aggregation processes in the suspensions. The major interparticle forces are of DLVO, patch-charge and steric origin depending on the type and the concentration of the aggregation agents. This is an important basis for the further formation of stable nanocarriers, hybrid LDH-latex porous materials or some efficient fire-retardants.

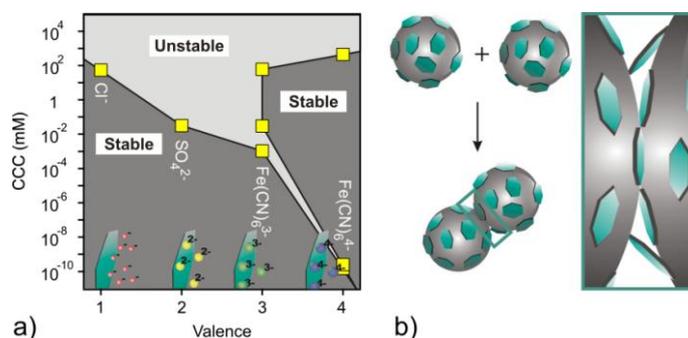


Fig 1. Stability map of LDH dispersions in the presence of counter-ions of different valence (a), graphical representation of patch-charge interactions during heteroaggregation process (b)

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# Multiple Light Scattering as a tool to monitor size evolution of nanoparticles during wet milling, comparison with laser diffraction and DLS

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Nano suspensions or emulsions are widely used in the industry but their real dispersion state remains unknown or not well characterized in their native and concentrated form. Indeed, it is well known that aggregation and agglomeration may exist in concentrated regime.

A technique of Static Multiple Light Scattering (SMLS) is proposed to measure mean particles size in a large range of concentration between 0.0001 and 95%, for sizes between 10 nm and 100  $\mu\text{m}$  by Turbiscan LAB technology. Turbiscan consists in sending a light source (880nm) and acquiring backscattered and transmitted signal. The signal intensity enables to measure directly the mean spherical equivalent diameter ( $d$ ), knowing refractive index of continuous ( $n_f$ ) and dispersed phase ( $n_p$ ) and the particles concentration ( $\varphi$ ) according to the Mie theory:

$$d = f(BS \text{ (or } T), \varphi, n_p, n_f)$$

with BS for Backscattering Intensity and T for Transmission Intensity.

This technique has the advantage to measure in one click, without sample preparation or dilution, the mean particles size and so the dispersibility efficiency particularly for concentrated suspensions. Other optical techniques such as DLS, PTA or laser diffraction can perform this measurement but only at a very high dilution which denatures the agglomerates and give an erroneous size of the native particles.

In this work, we present a complete study of size measurement of silica particles exposed to wet milling and going from micro to nanome nanometers. This size is measured with SMLS and compared with DLS and Laser Diffraction.

We propose also to present comparison of SMLS with SEM/TEM microscopy size measurement.

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# Chiral Plasmons as Biodetection Tool in Neurodegenerative Diseases

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Proteins such as beta amyloid and alpha synuclein have been shown to play a central role in the pathogenesis of common neurodegenerative disorders like Alzheimer's (AD) and Parkinson's diseases (PD) [1]. Protein aggregation leading to formation of fibrils is believed to be the critical step in the cause of these diseases. One of the major challenges is to detect the conformational changes and study the kinetics of fibril formation using suitable methods [2,3]. We demonstrate the use of gold nanoparticles as enhancing/retarding agents in protein aggregation and investigate the kinetics of the process through the formation of protein fibril-nanoparticle hybrid systems.

We synthesized novel hybrid conjugates based on protein fibrils as templates and gold nanoparticles as plasmonic materials. Suitable experimental conditions such as concentration, temperature and pH were optimized for the synthesis of helical one dimensional protein aggregates. The plasmonic metal nanoparticles are introduced on to these templates utilizing electrostatic and covalent interactions, leading to the formation of helical nanoparticle assembly on the protein fibrils. The kinetics of protein aggregation was also monitored by studying in situ the aggregation of proteins in presence of nanoparticles. The interaction between protein and plasmonic nanoparticles resulted in chiral plasmons, the intensity and position of which depended largely on the nature of interaction and the dimensions of the particles. The position of CD signals in the plasmonic region could be tuned by varying both the template as well as the nanoparticle. The observed plasmon chirality can be explained based on the coupled dipole model [4] wherein the strength of the dipoles and distance between the particles are crucial factors in deciding the nature of chiral signals. The hybrid system is further used for identification of different conformational states of proteins using Surface Enhanced Raman Scattering (SERS). This could be achieved through the monitoring of Raman signals of the protein in its monomeric and self-assembled states in the absence as well as presence of nanoparticles. Our ultimate aim is to utilize the hybrid chiral systems as biosensors for the detection as well as kinetic investigation of protein aggregation.

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# Membrane fusion induced by weak and specific interactions

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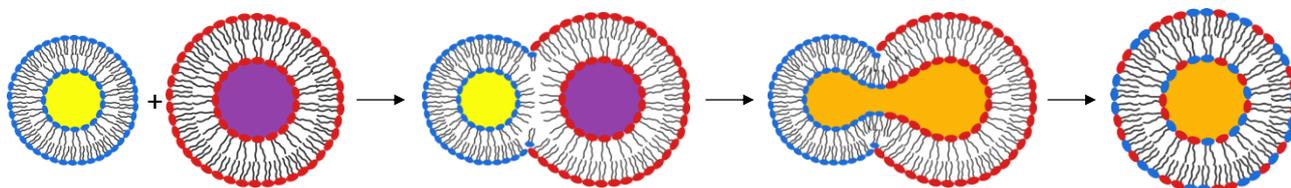
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Membrane fusion is an essential phenomenon in many cellular processes, including the entry of pathogens into host cells, the transfer of genetic material, the transport of newly synthesized membrane constituents [1-3]. It is defined as the process by which two different lipid membranes merge into a single continuous bilayer. Scientific community is very active in recent years to better understand the molecular events responsible for the intermembrane fusion. The control of the fusion between vesicles or bacterial membranes is a major issue in the development of drug delivery systems, the control of chemical reactions (bioreactors) or the development of artificial cell systems (Bottom-up approach of Synthetic Biology).

The model systems studied are phospholipid-based vesicles in order to mimic most biological membranes. The originality of this work is to incorporate a nucleotide lipid to promote and optimize the membrane fusion. This phenomenon is governed by the Watson-Crick base-pairing interactions between the complementary vesicles. Indirect techniques (dynamic light scattering, differential scanning calorimetry) have clearly shown the existence of a mixed post-fusion bilayer. The fusion event depends on the phospholipid/nucleolipid composition and the fluid-gel transition temperature. Direct visualization of this phenomenon is carried out by epifluorescence microscopy (including confocal microscopy) using fluorescent phospholipids. The fluorophores will also make it possible to label the bilayer in order to visualize microdomains (lipid raft) playing an important role in the membrane fusion.



**Figure 1** Membrane fusion.

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# The use of lipid sponge-like nanoparticles as carriers for macromolecules

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The advantage of using nonlamellar lipid liquid crystalline phases have been demonstrated in many applications, such as drug delivery, protein encapsulation or crystallization [1-4]. We have recently reported [5] that a mixture of mono- and diglycerides is able to form sponge-like nanoparticles (L<sub>3</sub> NPs) with up to 13 nm of aqueous pore size. This makes these systems suitable for entrapment of macromolecules. These large aqueous pore sizes are attributed to the introduction of the surfactant Polysorbate 80 (P80), which also aids the dispersion and stabilization of the L<sub>3</sub> NPs. Small Angle Neutron Scattering (SANS) experiments have here been performed in order to locate the P80 in the particle matrix.

In addition, the interfacial properties of the sponge-like nanoparticles are crucial for many applications and consequently, we have investigated their adsorption on hydrophilic silica by Quartz crystal microbalance with dissipation (QCM-D) and Neutron reflectivity (NR). Because this system is promising for the encapsulation of proteins, we will also present preliminary results on the adsorption of two proteins of different sizes (34 kDa and 460 kDa) in the lipid layers formed by the L<sub>3</sub> NPs. These experiments will help us to understand the nature of the interactions between the enzyme and the lipid. The results will be discussed in terms of the ability of these nanoparticles to encapsulate and release of the proteins in the lipid matrix.

**Acknowledgements** The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° 606713.

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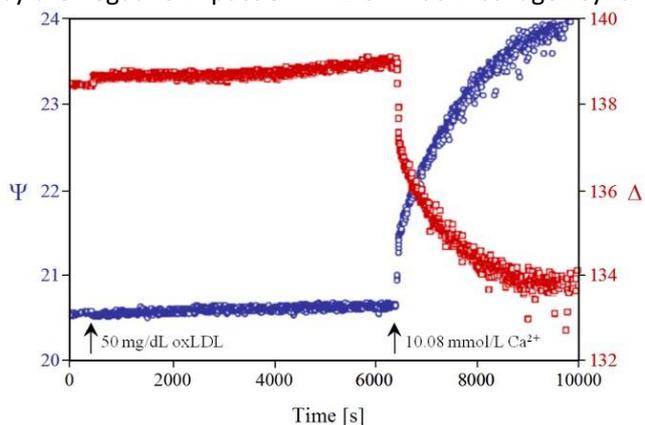
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# Atherogenesis and plaque rupture, surface/interface-related phenomena

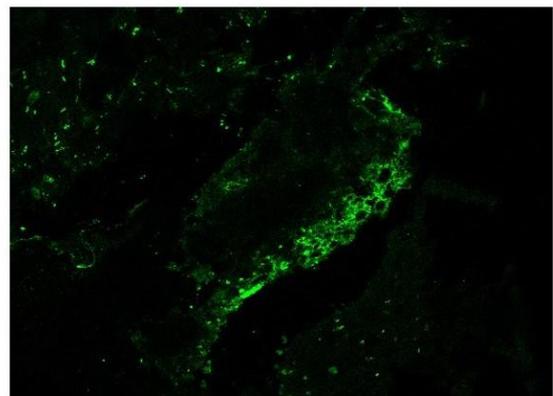
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**Background:** The morphological changes of arteriosclerotic blood vessels are caused by complex inflammatory and fibroproliferative processes leading to proliferation and migration of endothelial, vascular smooth muscle and white blood cells (monocytes) which, besides subendothelial lipid deposition, contributes to typical arteriosclerotic lesions known as plaques. On the molecular level, heterotrimeric nanoplaque formation can be interpreted as  $\text{Ca}^{2+}$ -driven lipoprotein binding to anionic biopolyelectrolytes of the proteoglycan type. Both transmembrane heparan/chondroitin sulfate proteoglycans HS/CS-PGs (syndecan superfamily) of endothelial and vascular smooth muscle cell membranes and extracellular matrix-integral heparan sulfate proteoglycans HS-PGs (perlecan, fibroglycan, glypican) have plasma lipoprotein binding domains strongly implicated in molecular nanoplaque formation (earliest stages in atherogenesis) and arteriosclerotic plaque rupture (possible final stage in atherogenesis). Their anionic polyelectrolyte nature favours  $\text{Ca}^{2+}$ -binding from the very beginning, which together with cytokine-driven fibroproliferation is prerequisite for fully blown up plaque formation over the years. Inflammation, ROS (reactive oxygen species) attack, disintegration and blood turbulences can lead to life-threatening plaque rupture at the blood–tissue interface. **Methods:** Nanotechnologic biosensor ellipsometry, photometric methods, ELISAs and EIAs were applied. Spatial distribution of PML (promyelocytic leukemia protein) and NF $\kappa$ B (nuclear factor kappa B) was assessed in cross sections (4  $\mu\text{m}$ ) of human coronary arteries using confocal laser scanning microscopy. Slides were analyzed by measuring their fluorescence. **Results and Discussion:** It is well-known that LDL is not so much responsible for arteriosclerotic plaque formation but its oxidized form oxLDL. Lipid peroxidation is the result of an action of ROS on the lipoproteins leading preferably to epoxides. In an ellipsometry experiment, oxLDL coating of a hydrophobized silica surface is diminished because of its highly negative charge density. On the other hand, oxLDL docking to HS-PG, coating the hydrophobized silica surface with its monomolecular layer, is very prominent and different from LDL docking. With  $\text{Ca}^{2+}$  addition, HS-PG/oxLDL/ $\text{Ca}^{2+}$  nanoplaques are formed. This process can also be recorded under *in vivo* conditions, when the silica surface is overgrown with a confluent monolayer of human umbilical vein endothelial cells expressing HS-PG on their cell surfaces (Fig. 1A). After a while, the adsorbed amount is steadily decreasing, since oxLDL attacks the linkage  $\beta$ -D-glucuronic acid  $\beta(1\rightarrow4)$  to *N*-acetyl- $\beta$ -D-glucosamine of HS. In the presence of ROS scavengers, this disintegration is slowed down or even halted. The presence of ROS generates inflammation and *vice versa*. In the inflamed tissue of an arteriosclerotic plaque, especially in the vulnerable shoulder region of the fibrous cap, PML seems to counteract this disintegration (Fig. 1B). PML is known to modify cell metabolism in various ways: inflammatory pathways, cell cycle regulation, apoptosis, senescence, transcriptional regulation, DNA repair and intermediary metabolism. As these metabolic functions are implicated in plaque formation, PML expression itself is modulated under stress conditions, such as inflammation. Moreover, PML had been shown to positively regulate cytokine signaling, reversely, a regulatory influence of PML in atherogenesis can be suggested. In a molecular biological approach, we show that in human coronary artery plaque ruptures (seen in explanted hearts after transplantation), PML is dramatically upregulated to combat ROS-induced plaque fibrous cap disintegration at this blood–tissue interface. **Conclusions:** ROS-induced oxLDL is decisively responsible in generating the very earliest stages of arteriosclerotic nanoplaque formation and also for disintegration in plaque rupture. A strong fibrous cap strengthening process, preferentially in the vulnerable shoulder region, seems to be mediated by molecular disinhibition through the negative effect of PML on NF $\kappa$ B followed by the negative impact of NF $\kappa$ B on matrix collagen synthesis.



**Fig. 1A.** Ellipsometric response ( $\Psi$   $\circ$  and  $\Delta$   $\square$ ) on addition of oxLDL to the cell-based substrate (nanoplaque formation).



**Fig. 1B.** Photograph of immunohistochemical staining of a human coronary arteriosclerotic artery (plaque rupture) with an anti-PML antibody (green).

# Mesomorphism and ionic assembly of 2D molecular blocks as potential nanowire precursors

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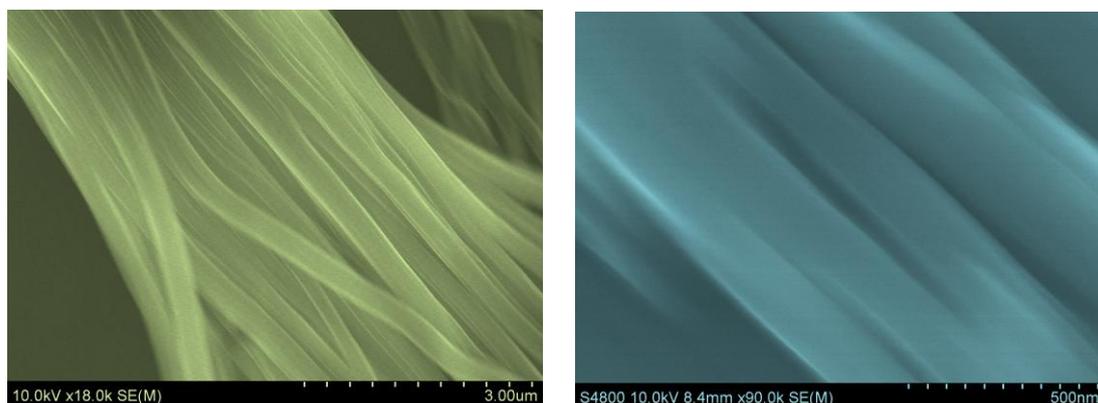
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Self-assembly is a versatile strategy for the bottom-up fabrication of nanomaterials with minimalist use of energy [1]. By playing with various types of non-covalent interactions, it is possible to construct diverse architectures by using molecular building blocks. Moreover, such building blocks may have functionalities that change synergistically from the monomer to the aggregated state. We present results on the self-assembly of porphyrins and phthalocyanines (2D molecules) into lyotropic liquid crystals in water (i.e. chromonics). Cationic and anionic porphyrins and phthalocyanines form nematic and hexagonal chromonic mesophases in water as confirmed by Small Angle X-ray Scattering (SAXS) measurements. The liquid crystals are constituted by oriented stacks with unimolecular cross-section similar to discotics [2].

Coupled aromatic  $\pi$ - $\pi$  and ionic interactions in oppositely charged porphyrins produce crystalline fibers with nanoscale diameter and several micrometers in length formed by bundles of molecular columns (see Figure 1). These assemblies show non-additive optical properties. The carbonization of the porphyrin fibers produces in turn carbon nanofibers at high yield and with interesting electrochemical performance. The potential of porphyrin ionic assemblies as templates for the fabrication of coated inorganic nanowires from different complexed heteroelements is also discussed.



**Figure 1** Scanning Electron Microscopy (SEM) images of as prepared ionically-assembled porphyrin nanofibers (left) and after carbonization at 1000 °C (right)

**Acknowledgements** C.R-A is grateful to the World Premier International Center for Materials Nanoarchitectonics (WPI-MANA, Japan) for the MANA Short-Term Invitation Program.

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# Synthesis and characterization of graphene oxide-polystyrene composite capsules with aqueous cargo via a water-oil-water multiple emulsion templating route

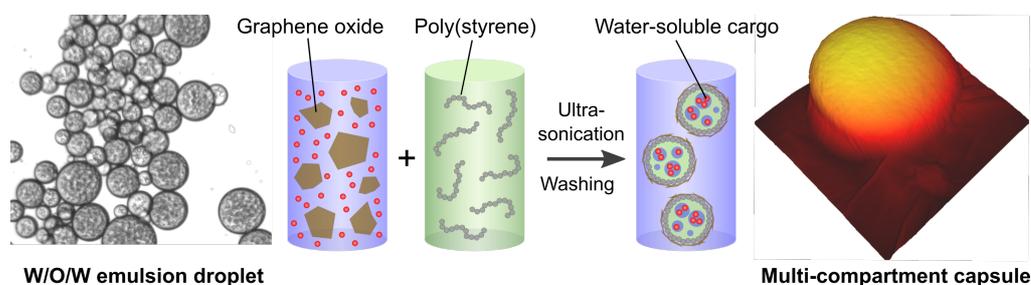
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Graphene oxide/polystyrene (GO/PS) nanocomposite capsules containing a two-compartment cargo have been successfully fabricated using a Pickering emulsion strategy [1]. Highly purified GO sheets with typically micron-scale lateral dimensions and amphiphilic characteristics were prepared from an oxidation reaction of graphite with concomitant exfoliation of the graphite structure [2]. These GO sheets were employed as a stabilizer for oil-in-water emulsions where the oil phase comprised toluene or olive oil. The stability and morphology of the emulsions were extensively studied as a function of different parameters including GO concentration, aqueous phase pH, ultrasonication time, effects of added electrolytes and stability to dilution [3]. In selected conditions, the olive oil emulsions showed spontaneous formation of multiple w/o/w emulsions with high stability, whereas toluene formed simple o/w emulsions of lower overall stability. Olive oil emulsions were therefore used to prepare capsules templated from emulsion droplets by surrounding the oil phase with a GO/PS shell. The GO sheets, emulsions and composite capsules were characterized using a variety of physical and spectroscopic techniques in order to unravel the interactions responsible for capsule formation. The ability of the capsules to control the release of a model active agent in the form of a hydrophilic dye was explored, and release kinetics were monitored using UV-visible spectroscopy to obtain rate parameters. The composite capsules showed promising sustained release properties, with release rates 11× lower than the precursor GO-stabilised multiple emulsion droplets.



**Figure 1** Schematic illustration of the PS/GO- microcapsule fabrication and encapsulation process with AFM image of the capsule.

**Acknowledgements** The financial support of Iraqi Ministry of Higher Education and Scientific Research (MOHESR) and Monash Centre for Atomically Thin Materials (MCATM) is acknowledged for supporting the facilities used in this research.

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# Effect of Additives to Control the Lamellar Bilayer Structure of a Cationic Surfactant

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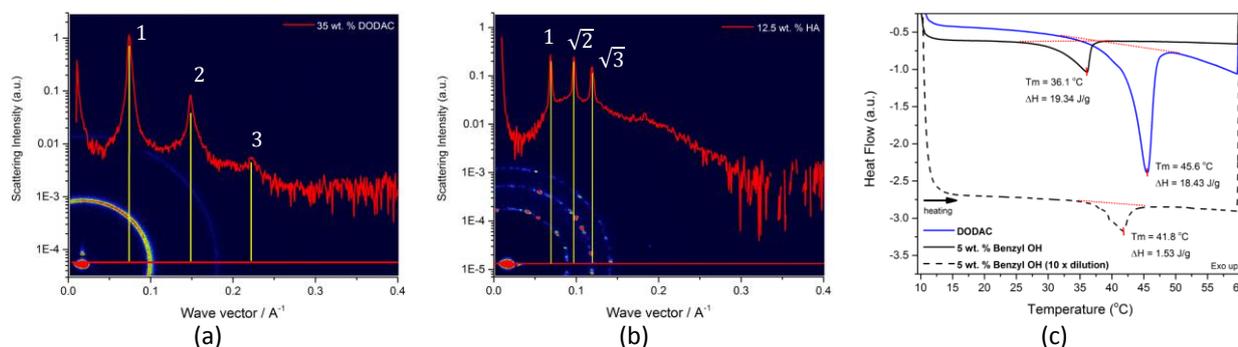
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It is well-known that double tail surfactants assemble in lamellar aggregates in aqueous solutions. Moreover, this class of amphiphiles is known by its swelling potential.<sup>1</sup> The gel-to-liquid crystalline phase transition temperature ( $T_m$ ) of dioctadecyldimethylammonium chloride (DODAC) surfactant system in the presence of additives is determined. Depending on the molecule, its location in the water phase, or at the interface a destabilization of the surfactant structure is observed resulting in a lower  $T_m$ .<sup>2</sup> Strikingly, also a transition from lamellar to a cubic phase is observed. In particular, we address the question on how the physicochemical characteristics of both surfactant and additive can tune the aggregate behavior. Small-wide angle X-ray scattering (SWAXS) was used to study the organization of the lamellar phase and its crystalline structure. Differential scanning calorimetry (DSC) studies provided the transition at which the “frozen” alkyl chains gain free movement due to its melted state. The observations indicate that there is a possibility to obtain a melted state,  $L\alpha$  phase, at a significantly lower temperature in the presence of an additive and suggest that it is possible to achieve a liquid crystal-to-gel transition by dilution.



**Figure 1** (a) Scattering pattern and 2D image of 35 wt. % DODAC-water binary system and corresponding Bragg diffraction peaks. (b) Scattering pattern and 2D image of DODAC-water-hexanoic acid ternary system (35-52.5-12.5 wt. %) and corresponding Bragg diffraction peaks. (c) Thermograms under heating for the samples 35 wt. % DODAC-water : 0 wt. % additive (full blue line); 5 wt. % benzyl alcohol (full black line); 5 wt. % benzyl alcohol after dilution (dash black line).

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# Thermodynamics of micellization: From one- to two-step model

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Micellization has been widely studied process and the value of critical micelle concentration, cmc, is regarded as one of the main characteristics at characterization of surfactants. However, cmc is well-defined for surfactants forming large micelles, whereas for surfactants with medium sized micelles cmc values are considerably dependent on the applied method. Consequently the same can be assumed for studies of thermodynamics of micelle formation process, based on the temperature dependence of cmc (van't Hoff approach). Perhaps the most precise methods to study thermodynamics are calorimetric methods such as isothermal titration calorimetry, ITC, which directly measures enthalpy changes, and differential scanning calorimetry, DSC, where changes in heat capacity are determined.

In this contribution, first the differences in thermodynamics of micellization between non-ionic and ionic surfactants studied by ITC will be demonstrated and then the nowadays challenges at the evaluation of thermodynamics of micellization for ionic surfactants will be presented. Next, a short overview of so far used methods for determination of thermodynamics parameters will be presented [1-4], with their main assumptions such as taking into account one equilibrium between monomers and micelles and some empirical parameters at data analysis are assumed. It turned out that one equilibrium model is applicable for surfactants with large average aggregation numbers over a wide temperature range however it is less suitable for the systems possessing smaller aggregation numbers changing significantly with temperature and concentration.

By representing micellization by the two-step model (Figure 1) the average aggregation number becomes indirectly temperature and concentration depended and such model can fit well the ITC experimental data of most ionic surfactants, as it will be demonstrated finally.

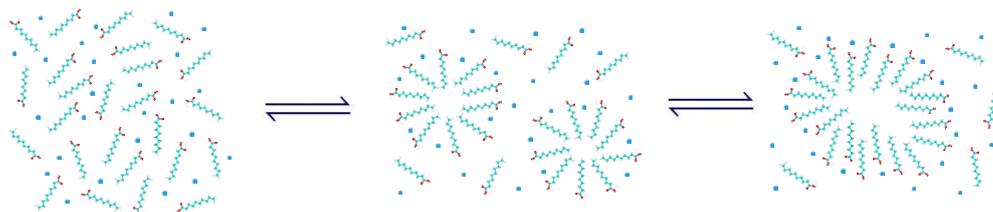


Figure 1 Two-step micellization model.

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# Multivariable reentrant condensation of microgel-polyelectrolyte complexes

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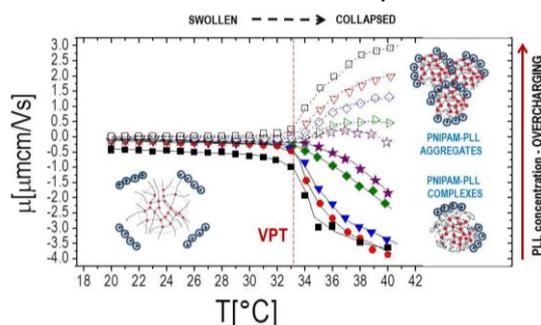
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Charged colloids and oppositely charged polyelectrolytes react spontaneously by electrostatic interactions with formation of self-assembled complexes, which may change considerably when different parameters, such as composition, ionic strength or preparation procedure, are modified. The comprehension of the underlying mechanism requires an extensive investigation of the interaction between oppositely charged macromolecules, which represents a fundamental problem in the field of self-assembly in soft matter. Polyelectrolyte adsorption onto oppositely charged surfaces represents the core of the problem since it drives overcharging and charge inversion phenomena [1]. Although the relevance of polyelectrolyte-colloid complexation has been established in a variety of systems undergoing self-assembly, its features have been always discussed in presence of colloids with fixed charge density.

Charged thermoresponsive particles with volume phase transition (VPT) give the opportunity to finely tune physical adsorption of polyelectrolytes simply by changing temperature, since VPT affects dramatically the charge density and polymer adsorption as well. Poly(N-isopropylacrylamide) (PNIPAM) is a well-known thermosensitive microgel system. It exhibits a significant VPT above the lower critical solution temperature (LCST), around 33°C in aqueous media [2]. Many studies have shown that the VPT can be modified by additives of inorganic salt, surfactants, ionic liquid and urea. Besides that, the VPT and swelling/deswelling behavior are also controlled by the introduction of charged groups to PNIPAM microgel networks, thus offering the opportunity to tune charge density just by changing the temperature.

In this work we exploit the unique features of PNIPAM microgels to study their complexation with  $\epsilon$ -polylysine ( $\epsilon$ -PLL) a short biocompatible polycation. We employ a combination of light scattering, TEM-AFM microscopy, electrophoretic and dielectric spectroscopy measurements to characterize  $\epsilon$ -PLL/PNIPAM complexes. We show that complexation is driven by the VPT of microgels and a large overcharging occurs only for  $T > T_{LCST}$  where bare microgels collapse and a negative electrophoretic mobility  $\mu$  is built. Polyelectrolyte adsorption gives rise to a reentrant condensation of microgels for  $T > T_{LCST}$ , as opposed to a continuous enhancement of particle condensation observed for monovalent salt. This peculiar electrostatically-driven controlled aggregation is here primarily tuned by the VPT-transition of PNIPAM and opens new intriguing scenarios for the controlled self-assembly of soft colloids.



**Acknowledgements** S. S. thanks E. Zaccarelli for scientific discussions and funding from ERC-MIMIC project

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# Responsive Hydrophobically Modified Poly(acrylates): Molecular Structure Effect

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Cristina-Florentina Mihailescu<sup>2</sup>, Roumen Todorov<sup>1</sup>, Ludmila Aricov<sup>2</sup>, Dan Florin Anghel<sup>2</sup>  
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Hydrophobically modified polyelectrolytes, such as poly(acrylates) are of a great academic and practical interest. Known for their peculiar behaviour at aqueous media and tunable rheological properties, they find wide application as technologic viscosifiers, emulsifiers, coagulants, etc. in various industrial processes. In this respect the present study explores the bulk and interfacial characteristics of liquid formulations based on hydrophobically modified polyacrylic acids in order to clarify their response to changes in the polymer molecular design under various experimental conditions.

Recently two specific types of polyacrylic acids have been synthesized: PAA25C<sub>12</sub> (MW=25000) and PAA150C<sub>12</sub> (MW=150000); both are randomly grafted with 3% (units/mol) dodecyl (C12) chains. Aqueous solutions of these polymers are investigated in view of possible further industrial applications. Bulk and interfacial experiments are conducted by simultaneously varying the pH of the solutions and the content of a low-molecular-mass electrolyte. The static and dynamic bulk rheological properties of the liquid systems are studied using Edinburgh Instruments F920 spectrofluorimeter and Kinexus Pro Rheometer (Malvern, U.K.) respectively. The dynamic, equilibrium and rheological properties of the adsorption layers at solution/air interface are also investigated by profile analysis tensiometer in a bubble mode (PAT-1, Sinterface). Experiments, concerning foam film characteristics (kinetic of film drainage, disjoining pressure vs. film thickness isotherms, stability, etc.) are conducted using the microinterferometric method of Sheludko-Exerowa and the Thin Liquid Film-Pressure Balance Technique.

The obtained results contain important novel information about the behaviour of the investigated systems in the bulk, at the solution/air interface and in foam films. The data are interpreted in terms of intramolecular/intermolecular interactions and changes in the molecular structure of the poly(acrylate), as well as the responsiveness to various changes in the experimental conditions (pH, presence of low-molecular-mass electrolyte, etc). The observations made give good reasons to believe that the possible applications of these poly(acrylates) to particular industrial innovations could be specified by choosing the polymer with the appropriate molecular design and through fine-tuning of the composition of the respective liquid formulations.

**Acknowledgements:** This work was carried out within the Bulgarian-Romanian joint research project for years 2015-2017 titled "Aqueous solutions of hydrophobically modified poly(acrylates)". The Romanian authors gratefully acknowledge the support of EU (ERDF) and Romanian Government allowing for acquisition of the research infrastructure under POS-CCE O2.2.1 project INFRANANOCHEM, No. 19/2009.03.01 and the support from PN-II-ID-PCE-2011-3-0916 grant. The Bulgarian authors are grateful for the financial help of Project BG05M2OP001-2.009-0023 funded by OP "Science and Education for Smart Growth" 2014-2020 of EU Structural Funds.

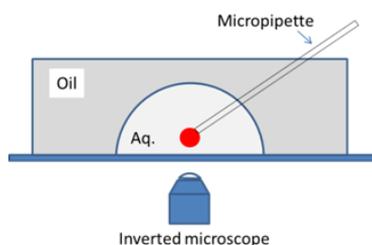
# Microgels for Drug Delivery: Loading and Release in Liquid Flows and Micro-drops

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Polyelectrolyte microgels are used as drug carriers for protein-, peptide- and amphiphilic drugs. In liver cancer therapy, drug loaded microgels with diameters of order 100  $\mu\text{m}$  are deposited in the blood vessels at the site of the tumor where they cause embolization following the swelling of the networks during drug release. This increases the efficiency of the therapy by reducing the flow of nutrients to the tumor and decreases side effects by limiting systemic spreading of the toxic drug. The swelling response and release kinetics depend on the strength of interaction between the network and the drug. For amphiphilic drugs it is expected to depend strongly on their self-assembling properties and distribution inside the microgels [1, 2]. We will show how detailed information about the mechanisms of drug loading and release can be obtained from a combination of microscopy studies of single microgels in liquid flows and in microscopic drops [3] and structural information from SAXS. The methods will be illustrated by examples from systematic studies of combinations of anionic microgel networks (including polyacrylate, hyaluronate, poly(styrenesulfonate), and commercial DCBead) and a number of different cationic amphiphilic drugs, regular surfactants, and proteins. We will also present evidence of electrostatically driven spontaneous core-shell segregation of protein-rich and surfactant-rich phases in single microgels, interesting for encapsulation of protein drugs.



*Schematic of micro-drop experiment*



*Microscopy image of core-shell segregation of protein (red) and surfactant phases in microgel*

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# Formulation and characterization of hydroxypropyl guar based gel-like systems, tailored for the low impact cleaning of works of art surfaces

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The development and characterization of a new family of water based gel-like systems containing hydroxypropyl guar gum (HPG) with borax as crosslinker are presented in this contribution. In the formulation glycerol is introduced as plasticizer, and its role is broadly investigated. The effect of the components on the structure, on the viscoelastic behavior of the system and on the activation energy related to the relaxation process has been investigated by means of rheology, Nuclear Magnetic Resonance (NMR) and Small Angle X-ray Scattering (SAXS) [1-2]. Results indicated that the mechanical properties of the systems can be tuned by varying the amount of each component; <sup>11</sup>B-NMR and <sup>1</sup>H-NMR measurements highlighted the role of glycerol in the crosslinking mechanism, with the formation of a glycerol-borate complex. The characterization approach is used to identify the best formulation, in the view of a future application in the field of cultural heritage conservation, in particular for the cleaning of surfaces of historical and artistic interest [3]. The main goal is to obtain a system adaptable to the roughness typical of surfaces of many artifacts. The best formulation was used for preliminary cleaning tests on a *stucco* artifact deriving from the decorations of *La Fenice* theatre, in Venice. The tests suggest a promising efficacy in selective cleaning of the surface and make these materials particularly interesting in the field of restoration.



**Figure 1:** On the left, Storage modulus values at Frequency=1Hz (■) and Crosslinked Borate Area obtained from NMR measurements (▲) are plotted against glycerol concentration. Pictures on the right show the *stucco* surface before (A) and after (B) the cleaning, with the comparison between the the HPG based system (1) and a wet cotton swab (2).

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# Directing structure in colloidal liquid crystals with patchy rod-like particles

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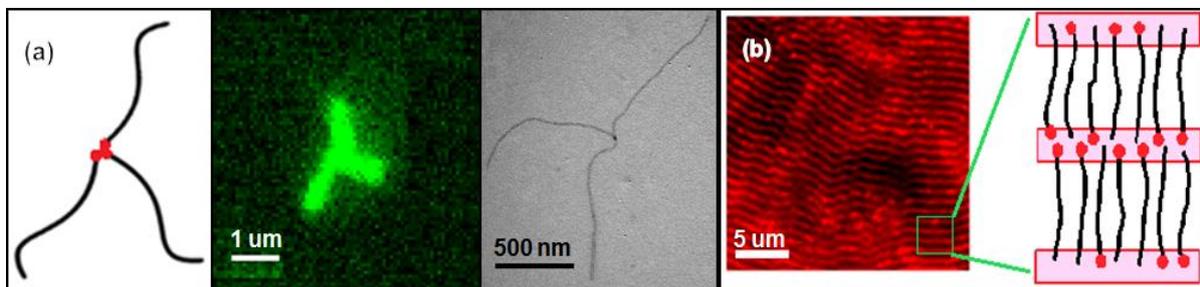
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Fd virus, as a model system of rod-like colloid, motivate a strong interest in soft condensed matter. The micrometer length scale of fd allows for direct observation at single particle level thanks to optical microscopy methods [1]. By varying concentration of these viral polyelectrolyte particles in aqueous suspension, several liquid crystalline phases can be formed: cholesteric, lamellar (or smectic) and columnar mesophases [2].

In our study, we go beyond hard-core interaction between rods, and investigate the self-organization of virus suspension where directional attractive interactions are introduced. Using regio-selectivity chemistry, one end of fd virus can be functionalized with red fluorescent dyes which act as a hydrophobic patch due to the presence of aromatic rings and therefore induces regio-localized attraction between tips of the rods (Fig. 1a). In diluted regime, our chemically modified particles form multiarm structures of tunable valency. At higher concentration, virus end attraction results in the extension of lamellar phase range (Fig. 1b).

Structural properties of virus suspensions exhibiting these patchy inclusions are investigated and recent results on optical microscopy, transmission electron microscopy and X-ray scattering experiments will be presented.



**Figure 1** (a) Star-like structure (trimer) formed by three patchy fd viruses. Left: Schematic view, the red dot represents red fluorescent dyes; Middle: Fluorescence microscopy image; Right: Transmission electron microscopy image. (b) Fluorescence microscopy image of viruses self-organized into a smectic phase; Schematic represents two smectic layers.

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# Optically Active Liquid Crystal Coatings containing Plasmonic Colloids

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The ability of liquid crystals (LCs) to spatially organize and orient micro- and nanoparticles (NPs) has been attracting the scientific community over the past two decades [1-3]. The synergetic properties of LC/plasmonic NP composite materials could find application in active glazing with thermochromic, electrochromic, and solar control properties [4].

Smectic A LCs possess a structure in layers. When confined between two surfaces promoting antagonistic (parallel and perpendicular) orientations of the layers, smectic A LCs may form defect patterns such as toric focal conic domains (TFCDs) (Figure 1). In particular, TFCDs have recently been shown to be efficient traps for quantum dots, and hence, templates for their organization [5].

In the present study, we focus on smectic A LC coatings with TFCD patterns with or without plasmonic NPs. Coatings are deposited at the surface of glass. To the best of our knowledge, such colloidal coatings have not been formulated so far. Firstly, we study for the first time the wavelength-dependent scattering properties of TFCDs in smectic coatings with different TFCD surface densities and sizes (Figure 1). Secondly, we investigate how plasmonic NPs orient and organize in such coatings, and how they impact the optical properties.

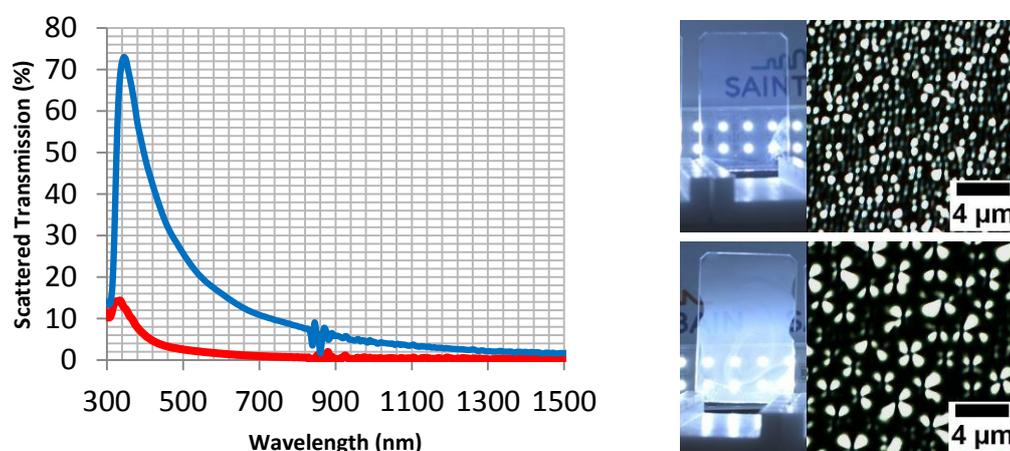


Figure 1 – Scattered transmission as a function of wavelength (left graph) of smectic A coatings on glass substrates (right pictures). The red (respectively blue) curve corresponds to the top (respectively bottom) smectic A coating, with small (respectively bigger) TFCDs, appearing as Maltese crosses under a polarizing optical microscope.

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# Structure and properties of hydrogels formed by polyelectrolyte complexes of $\kappa$ -carrageenan with gelatin

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Biopolymer gels are widely used in modern food technologies. The creation of compositions based on biopolymer systems that provide the necessary rate of gelation and the rheological properties of the final product is an actual issue that has both scientific and applied significance. Mixtures of gelatin (the product of triple helical collagen denaturation) with polysaccharides due to the ability to thermo reversible gel formation and the synergism of gelation properties are promising for use in various new technologies.

The paper summarizes the results of experimental studies of a new type of gelator – polyelectrolyte complex (PEC) formed by anionic polysaccharide of marine origin ( $\kappa$ -carrageenan) with gelatin in the aqueous phase. The data of <sup>1</sup>H NMR, FTIR and UV spectroscopy and scanning electron microscopy on the physical gelation process under conditions of complex formation are analyzed [1]. <sup>1</sup>H NMR data were interpreted in terms of the changing roles of electrostatic interactions, hydrophobic interactions and hydrogen bonds when PECs are formed. The time dependence of NMR signals intensities shows that the kinetics of gel formation consists of classical 'fast' and 'slow' periods, corresponding to a coil→helix transition and subsequent aggregation of helices. FTIR spectroscopy data show a sharp increase in the proportion of helical sections of gelatin  $\alpha$ -chains with an increase in the concentration of  $\kappa$ -carrageenan.

A critical value of  $\kappa$ -carrageenan/gelatin mass ratio is found. Increase in  $\kappa$ -carrageenan concentration above this value leads to dramatically changes in mechanism of gelation and supramolecular gel structure in comparison with those of native gelatin gel. The formation energies of  $\kappa$ -carrageenan-gelatin PECs, calculated by method of molecular docking, are consistent with the experimental data.

The studies of structural features of hydrogels are considered as a key to understanding the possibility of directed regulation of the gel rheological properties. Various types of rheological behavior of hydrogels formed by  $\kappa$ -carrageenan-gelatin PEC of different composition under conditions of shear deformation at constant shear rate and in dynamic analysis mode are considered [2].

Increasing  $\kappa$ -carrageenan concentration accelerates the gelation and leads to significant increase in the viscoelastic parameters of the PEC gels. At the  $\kappa$ -carrageenan/gelatin mass ratio above the obtained critical value non-linearity of viscoelastic properties becomes evident in much lower deformations in comparison with gelatin gels. The strength of gels characterized by the yield stress also increases along with  $\kappa$ -carrageenan concentration. The melting temperature increases for high  $\kappa$ -carrageenan/gelatin mass ratio.

A proposed models of the  $\kappa$ -carrageenan–gelatin complexes are discussed. It is hypothesized that at low concentration of PECs the hydrogel structure network is stabilized by inter-molecular triple helices of gelatin while at higher concentration of PECs (at  $\kappa$ -carrageenan/gelatin mass ratio more than obtained critical value) the structure is stabilized by three types of nodes: triple helices of gelatin and intra- and inter-molecular double helices of  $\kappa$ -carrageenan.

**Acknowledgements** The work was supported by Russian Science Foundation (project No. 16-16-00076).

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# Biodegradable emulsions using PLGA nanoparticles: structure and physico-chemical study

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Emulsions stabilized with poly(lactic-co-glycolic) acid (PLGA) nanoparticles (NP) offer the advantage, besides their stability, of avoiding the use of synthetic surfactants that may raise toxicity and environmental issues. We formulated fully biodegradable and biocompatible emulsions for pharmaceutical or cosmetic purposes stabilized with pure poly(lactic-co-glycolic) acid (PLGA) nanoparticles (NP), *i.e.* without any other polymer or surfactant, and with medium-chain triglycerides (Miglyol 812 N) as the oil phase. These emulsions were then compared with emulsions using the same oil, but formulated with PLGA-PVA NP, *i.e.* with polyvinyl alcohol (PVA) as NP stabilizer. Strikingly, depending of the type of NP used, the emulsions demonstrated very different structures at macroscopic, microscopic and interfacial scales. Indeed, with the same oil ratio, the emulsion layer was significantly thicker when using PLGA NP rather than PLGA-PVA NP. This was attributed to the fact that PLGA NP unexpectedly led to the formation of multiple W/O/W emulsions using a single step of emulsification, whereas simple O/W emulsions were obtained with PLGA-PVA NP. The latter NPs were more hydrophilic than pure PLGA-NPs because of the presence of PVA at the NPs surface. Moreover, PLGA NP did not significantly lower the interfacial tension, contrarily to PLGA-PVA NP. The chains on the surface of the PLGA-PVA NP were probably able to desorb from the NP and anchor at the oil/water interface, inducing an interfacial tension decrease. Finally, whatever the type of NPs used, they were adsorbed at the interface without influencing the rheological behavior of the interface.

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# Controlling surface coverage in Pickering systems: A double emulsion templating approach

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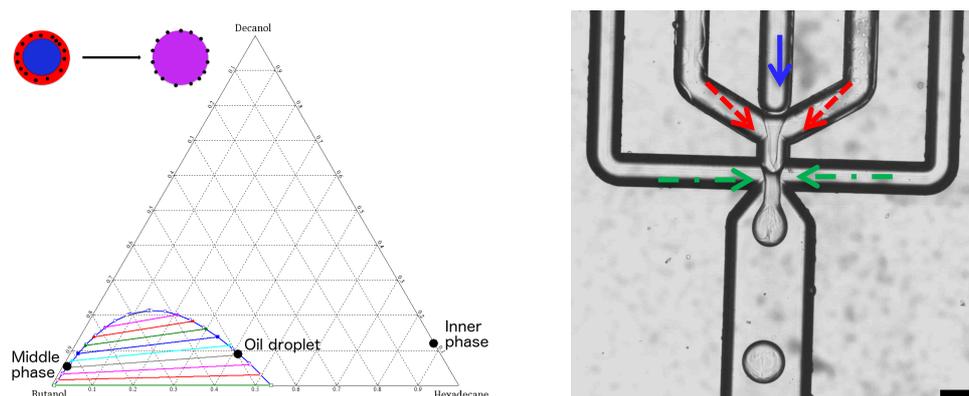
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Particle-stabilized emulsions, also called Pickering(-Ramsden) emulsions, are of interest due to their high stability against coalescence and Ostwald ripening. Whereas several factors may contribute to the stability of such systems, the mechanical properties of the interface clearly play an important role [1, 2]. Often, it is assumed that limited coalescence leads to densely packed, jammed interfacial layers and this imparts stability to the Pickering drops [3]. However, there are also literature reports that show that macroscopic stability of the emulsion can be achieved at low surface coverages when an aggregated structure is present [4]. To further enhance our understanding, we need a technique to control the droplet surface coverage. In the present work, we propose a novel strategy to generate droplets with a controlled surface coverage based on a microfluidic droplet generator and a Double Emulsion Templating Approach (DETA).

The proposed strategy produces controlled particle-laden oil droplets by using mixtures of two miscible fluids as the inner and middle fluid in a double emulsion template as illustrated in Figure 1. The middle and inner fluid are initially on opposite sides of the binodal region of a ternary phase diagram, and are chosen such that the middle phase dissolves into the inner one, ideally while maintaining an interface throughout the process. The particles are dispersed in the middle fluid, which has an intermediate polarity. By changing the particle concentration in the middle phase and the ratio of the flow rates between the phases, the surface coverage can be controlled. The validity of this approach is confirmed for several fluid and particle ratios where stable drops can be created and even extracted from the microfluidic chip. Due to the generic nature of this strategy, the effects of particle coverage and particle interactions on morphological processes can now be studied rigorously.



**Figure 1** Double Emulsion Templating Approach. The middle phase (red) contains the particles and dissolves in the inner phase (blue) which makes up the final droplet. Scale bar = 250  $\mu\text{m}$ .

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# Inverse Isasomes: From Aqueous To Oleaginous

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Decades of scientific research and applications have shown the importance of amphiphilic molecules as surfactant or self-assembly material with intriguing properties. The majority of the research was done in aqueous systems and the understanding of the behavior of such molecules is well investigated and understood. [1] Interactions of nonionic micelles (e.g. Pluronic) in water can be discussed with the hard sphere model where the collective diffusion increases with the concentration [2], but investigations of reverse nonionic micelles (e.g. sucrose esters) in oil showed a decrease in the collective diffusion. [3] This leads to the conclusion that interactions with solvent are very different in water and oil phases.

Internally self-assembled particles (isasomes like cubosomes, hexosomes etc.) were already described in 1989 [4]. Isasomes are oil-in-water emulsions, where the oil droplets are kinetically stabilized with the help of a polymeric or particle stabilizer and the interior of the oil droplet has a self-assembled liquid crystal structure that is in thermodynamic equilibrium. The structure can be tuned by the variation of the temperature or composition, like oil content to form a bicontinuous cubic, hexagonal and sometimes discontinuous micellar cubic phase. [5,6] Since then a huge body of literature and numerous applications arose, but all of them are based on a hydrophobic liquid crystal in excess water.

In this work we show the development and investigation of the reversed system, i.e. inverse isasomes: a hydrophilic liquid crystal dispersed in excess oil. A suitable hydrophilic liquid crystal was already described by Aramaki et al. [7], and is used as the basis for our new system. To find a suitable stabilizer is a more complex task. There are a few surfactants that allow the formation of water in oil emulsions with alkanes as oil, but to form a stable liquid crystalline phase in an alkane (tetradecane) has not yet been reported. To our knowledge such a stabilizer, if polymeric, has to show a high molecular weight and a low HLB so it will not disturb the interior structure. Since the molecular interactions in alkane are much weaker than in a polar system the prediction of such a system is difficult. In this contribution we report our results with in-house synthesized or commercial polymeric and particle stabilizers.

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# Surfactant self-assembly in deep eutectic solvents

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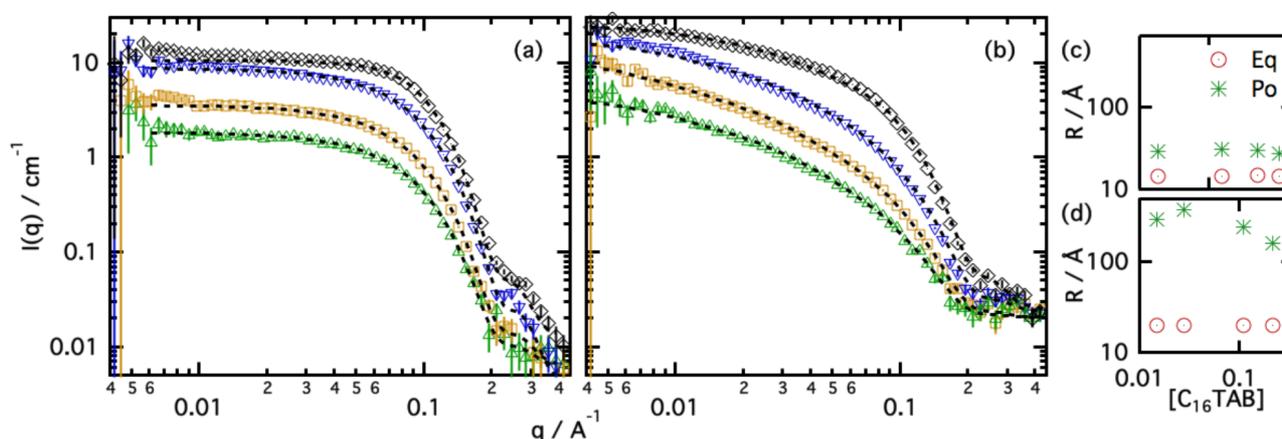
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Deep eutectic solvents (DES) are green solvents obtained through the complexation of a halide salt with a hydrogen bond donor at a certain mole ratio. Combinations of precursors allow myriad possibilities to be obtained in terms of physicochemical properties of the solvent, enabling solvent properties to be tuned for particular applications.[1] Our recent studies have shown the ability of DES to sustain self-assembly of surfactants.[2,3] Such alternatives bring the possibility to develop new, sustainable media for surfactant templating, microemulsion formation and bottom-up synthesis of nanostructured materials. These results have shown the formation of micelles with different morphologies than those surfactants in water and other polar solvents, promoting shape transitions that are uncommon in water.[4]

Here we will explore the effects of headgroup solvation on micelle morphology, counterion binding and the role of surfactant-solvent interactions in the surfactant micellisation. Surface tension, differential scanning calorimetry, small-angle neutron and X-Ray scattering were used to investigate the behaviour of anionic, cationic and zwitterionic surfactants in different DES. Our results provide a novel approach for surfactant aggregate manipulation in the absence of water. Selective charge screening at the headgroup region was found in particular systems. This change in the interfacial charge density, and therefore in micelle morphology, was found to depend on the surfactant concentration and solvent characteristics (Figure 1). Aiming to understand the fundamentals of amphiphile behaviour in these solvents, we will present details of surfactant self-assembly with varied physicochemical properties of the solvent, surfactant characteristics and the effects of counterion condensation.



**Figure 1** Small-angle neutron scattering data and fits of equivalent concentrations of  $C_{16}TAB$  in (a) 1:2 choline chloride:glycerol and (b) 1:1 choline chloride:malonic acid. Equatorial (Eq) and polar (Po) radii of  $C_{16}TAB$  micelles in (c) choline chloride:glycerol and (d) choline:malonic acid DES.

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# Fast liquid sheet and filament dynamics in the fluid splitting process

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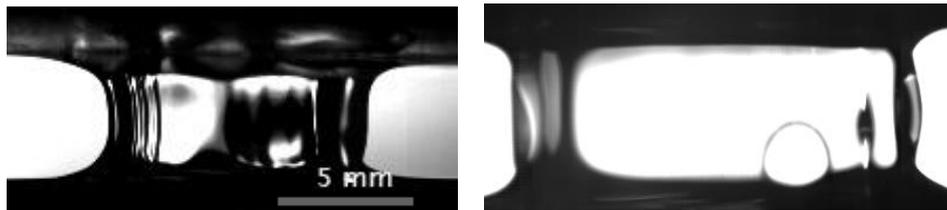
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Stretching of a liquid filament or jet is a part of many industrial processes, like printing in rapidly running gravure and flexographic (letterpress) printing machines, atomization or process engineering. Liquid filament/sheet stretching is also an element of rheological measurements, governed by inertial, viscous and capillary forces.

In the present study we consider the splitting dynamics of a small fluid drop entrapped between two parallel solid plates, which are rapidly pulled apart with an acceleration of up to  $200 \text{ m/s}^2$  such that a free liquid sheet is formed between them for a few milliseconds [1]. The velocities, time scales and shear rates in the experiment correspond to typical conditions encountered by printing ink at the lift-off of the print cylinder from the substrate.

Using high-speed video techniques we observe the formation and collapse of the liquid sheets and the subsequent filaments formed filaments (Fig. 1). We study the surface waves on both the sheet and the filaments. These are mostly emitted from the Taylor rim formed at the edge of the sheet. Depending on the Laplace number they propagate along the surface. However, if the rim contraction is faster than wave propagation velocity then the wave propagation is no longer detected. The fastest dynamics is that of capillarity-driven expansion of holes which occasionally appear in the liquid sheets [2,3]. The usual sheet thickness of 100-200 nm at the instant of breakup is measured. The measured expansion rates are anisotropic due to the fast sheet stretching.

Due to the surface tension the contracting rims accelerate rapidly towards each other, gathering the liquid in more or less massive border filaments. Depending on the capillary number, the collision of the two filaments may either result in a smooth unification, or in a highly dynamical collapse and a random emission of small liquid droplets.



**Figure1.** Left: a liquid sheet forming between a pair of parallel solid plates expanding rapidly in the vertical direction. Capillary waves are emitted from the filaments formed at the left and right borders. Right: A hole that has formed in the liquid sheet is expands rapidly. From its growth rate we can estimate the sheet thickness as approx. 200 nm.

**Acknowledgements.** We kindly acknowledge the financial support by the German Research Foundation (DFG) within the Collaborative Research Centre 1194 “Interaction of Transport and Wetting Processes”, projects A03 and C01.

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# Stabilizing emulsions with hydrocolloids: the case of Arabic gum

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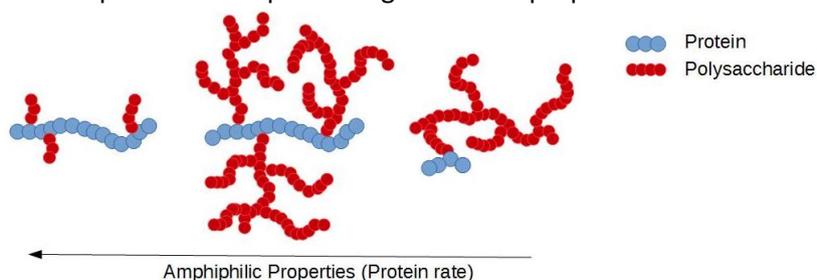
Hydrocolloids, are complex biopolymers mixtures corresponding to different masses and amphiphilicities, which originates from proteinaceous moieties linked to hydrophilic backbones. Using hydrocolloids for their interfacial properties, thus presents a challenge since the interfacial composition may largely differ from the bulk composition. Here we will discuss the case of Arabic gum, a natural product used as a stabilizer in formulations especially emulsions. Nonetheless, formulations remain empirical and we still lack straightforward composition/structure/function relationships for such systems.

In the literature, arabic gum was divided into three main fractions: polysaccharides, glycoproteins and protein/polysaccharide conjugates [1]. Conjugates were described as the good stabilizing specie when formulating emulsions. In fact, we show that all the species contain a protein fraction and thus are amphiphilic. Moreover, no limited coalescence regime was observed when the conjugate was in insufficient amounts to cover interfaces, despite its large adsorption energy. We instead observe a slow and continuous coalescence of emulsions, over weeks, contrasting with the expected behaviour of Pickering emulsions [2], which supports a continuum of amphiphilic species in the gum.

We developed methods, to separate the different species of the gum according to their size and amphiphilic property, to elucidate their contributions to emulsion stabilization. Emulsion-mediated separation, coupled with liquid chromatographic analysis, shows which species adsorb at oil/water interfaces as a function of gum concentration, pH and salinity. Furthermore, emulsion-mediated separation is also an easy and quantitative purification method, which makes it possible to obtain in large amounts the most amphiphilic fraction of the gum, in contrast to preparative chromatography methods.

We identified which physico-chemical parameters influence the adsorption of Arabic gum amphiphilic species at oil droplets surface and thus impact the metastability of emulsions over time. For instance, salt addition improves the stability of emulsions and macromolecular adsorption at the interface. This was confirmed with interfacial tension measurements and elucidated through SAXS measurements. Most species of the gum are shown to adsorb at the interfaces but their stabilizing properties largely vary due to differences in steric repulsion barriers.

Arabic gum must thus be viewed as a continuum of amphiphilic species with different properties (figure), which should help rationalize formulations using this original gum. Our work also opens new perspectives in the use and analysis of complex mixtures possessing interfacial properties.



**Figure:** Arabic gum is a mixture of macromolecular species with different sizes and amphiphilic

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# Highly efficient drag reduction mechanism by giant gas cavities

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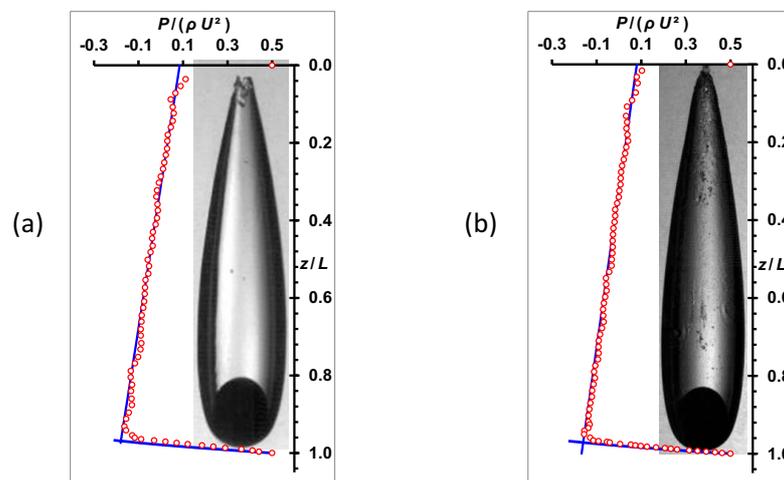
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Minimizing the retarding force on a moving solid sphere in liquid is the benchmark problem in the evaluation of design strategies to reduce friction and drag. A common approach is to modify the usual stick boundary condition of fluid flow at solid surfaces to facilitate liquid slippage or to reduce the tangential stress along the solid surface. Previous attempts include the use of bubble injection near surfaces [1], superhydrophobic surfaces [2-4], hot Leidenfrost surfaces [5-8] to sustain a sub-millimeter gas layer at a solid solid. However, the limited gas thickness produced by these methods only resulted in partial slip conditions.

Here we employ a class of self-determined streamline structure with a free slip surface that is made up of a giant gas cavity that completely encloses a metal sphere. Such a stable gas cavity is formed around the sphere as it plunges at sufficiently high speed into the liquid – water or fluorocarbon, held in a deep tank. If the sphere is either above the Leidenfrost temperature of the liquid or if the sphere surface is rendered superhydrophobic in water, the liquid will not be in contact with the sphere. The giant sphere-in-cavity structures are nearly neutrally buoyant. The cavity volume, between 5 to 15 times that of the sphere, is proportional to the density ratio of the sphere to the liquid. Its self-determined shape is consistent with the Bernoulli equation of potential flow applied at the cavity surface. The sphere-in-cavity experiences near zero drag and its fall velocity is not arbitrary but its square is proportional to the sphere diameter and the density ratio of the sphere to the fluid, therefore, larger cavities have higher characteristic velocities.



**Figure 1** Cavities around 20 mm Leidenfrost spheres (a) steel in water, (b) tungsten carbide in fluorocarbon liquid, PP1.

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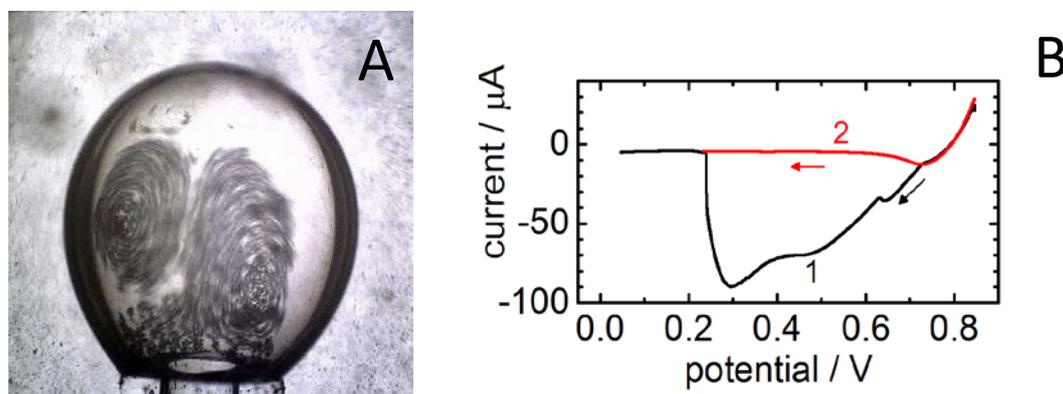
# Visualization of the interfacial turbulence at the electrochemically polarized liquid-liquid interface

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Interfacial turbulence frequently accompanies mass transfer across the interface between two non-equilibrated liquids [1]. This paper reports the visualization of the interfacial turbulence developed at the electrochemically polarized interface between an aqueous solution of NaCl and the solution of an organic background electrolyte in 1,2-dichloroethane (DCE) containing sodium tetraphenylborate [2]. The turbulence leads to a remarkable amplification of the faradaic current (polarographic maximum) associated with the transfer of the non-adsorbing Na<sup>+</sup> ion from DCE to water, which is observed at both the electrolyte dropping and sessile aqueous drop electrodes. Interfacial turbulence is visualized by using the graphite micro-particles suspended in DCE as a fluid flow tracer. Visualization reveals the rotating surface structures apparently giving a drive to the adjacent solution layer and to the solution streaming around the drop in the same potential range. A snapshot of the rotating circular surface structures at the sessile drop is shown in Fig. 1 (panel A). Faradaic current enhancement is demonstrated in Fig. 1 (panel B), which shows the initial (line 1) and succeeding (line 2) voltammogram of the Na<sup>+</sup> transfer at the sessile electrolyte drop. The decrease of the faradaic current from the enhanced (line 1) to the diffusion-controlled level (line 2) indicates that the interfacial instabilities have only transient nature and are induced only at the beginning of the newly formed drop and then quickly vanish. Observed phenomena are likely to play a role in the largely unexplored emulsification of the interfaces between two immiscible electrolyte solutions (ITIES), or the fusion of the emulsion particles with the ITIES.



**Figure 1** (A) Snapshot of the polarized aqueous sessile drop (diameter ca. 1.3 mm) in DCE with the rotating circular surface structures visualized by the adsorbed graphite micro-particles. (B) Initial (1) and succeeding (2) voltammogram (5 mV/s) of the Na<sup>+</sup> ion transfer from DCE to water. Concentration of Na<sup>+</sup> in DCE: 0.5 mmol/L.

**Acknowledgements** The financial support of the Czech Science Foundation (project number 17-09980S) is acknowledged.

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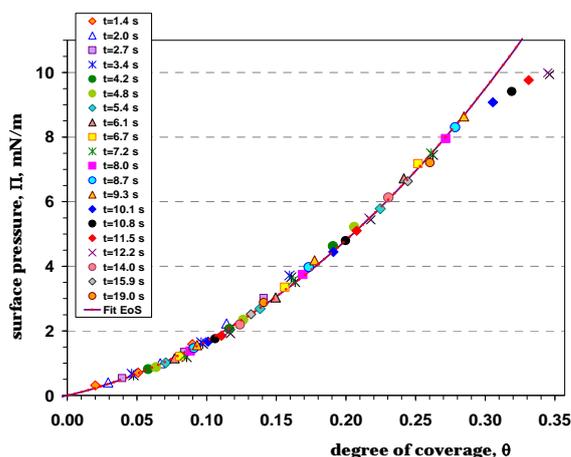
# Kinetic effects in the interfacial rheology and the adsorption, in systems containing proteins, polymers, and surfactants

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We discuss three dynamic aspects in the behavior of layers on surfaces between fluid phases. (i) Aggregated entangled network of protein (Hydrophobin) forms elastic layers of inhomogeneous thickness, which exhibit relaxation effects. The elasticity and the interfacial tension depend on the magnitude and the rate of deformation, as well as upon the operational pre-history. The observed relaxation phenomena can be explained by lateral redistribution of molecules by migration (surface diffusion), between lumps/ agglomerates and the spread layer [1]. (ii) With polymer/ surfactant mixtures, layers can be formed by attachment of polymer molecules onto the adsorbed surfactant. This can lead to inability of a certain fraction of the surfactant species to be exchanged between the interface and the bulk (sub-surface). Rheological studies by cyclic deformations of compression/ expansion reveal the macroscopic manifestation of different behavior of the reversibly and irreversibly adsorbed molecules. Gibbs' and mechanical elasticities are distinguished; the „apparent” viscosity is connected quantitatively with the kinetic coefficient of mass transfer to/from the interface. (iii) Surfactant layers are often characterized by the 2D equation of state (EoS: adsorption – interfacial tension relation); we found a way to obtain it from dynamic data (i.e., without going close to equilibrium). Under certain conditions, the kinetics of adsorption obeys specific laws of dependence upon concentration and time, which allows data representation in the form of a master curve (Fig. 1). The EoS is determined by fitting of the latter curve, whence some material constants are obtained. In addition, the adsorbed amount of surfactant vs. time,  $\Gamma(t)$ , is also acquired quantitatively; thus, one avoids the necessity of measuring it directly, which is rather difficult.



**Figure 1** Surface EoS [2], with two adjustables: one parameter of lateral interactions, and a constant for correspondence of the adsorption,  $\Gamma$ , to the theory. The fitted measurements refer to the non-ionic surfactant  $C_{10}EO_4$ .

**Acknowledgements** The financial support of the Horizon 2020 project ID: 692146-H2020-eu.4.b “Materials Networking” is gratefully acknowledged.

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# Standardization of iron oxide nanoparticles surface by oleic acid/DMSA ligand exchange reaction for advanced biomedical applications.

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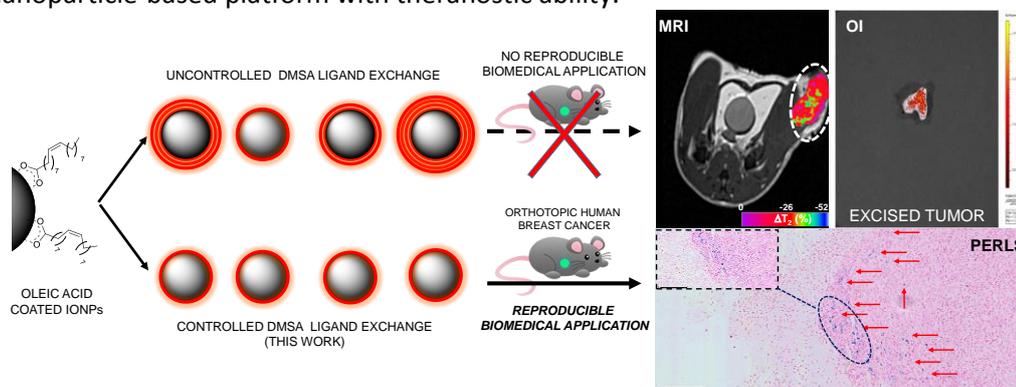
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Since the interactions of iron oxide nanoparticles (IONPs) with physiological environments are mediated by their colloidal properties and surface coating, the quality and reproducibility of the IONPs' surface is a crucial parameter for their successful biomedical application and clinical potential translatability. To date, a variety of synthetic methods have been applied to produce IONPs ranging between physical, chemical and biological methods. However, in many cases as critical drawback, the resulting ferrofluids are only stable in hydrophobic media (generally showing an oleic acid coating as stabilizing agent). Therefore, for biological applications, an intermediate phase transfer to aqueous media is mandatory. Within the surface coating reactions, the oleic/dimercaptosuccinic acid (DMSA) ligand exchange is one of the most widely used. However, this surface coating reaction has not been yet fully characterized and optimized. As consequence, the potential biological activity of DMSA-coated IONPs further modified with bioactive compounds will be highly unpredictable.

To this scope, herein, we elucidate the mechanistic aspects of OA/DMSA ligand exchange on IONPs and present a standardized protocol that enables controlled and reproducible DMSA shell grafting. After the synthesis and characterization of DMSA-coated IONPs of 10 nm core, by means of chemical strategies, we investigated the aspects hampering the reproducibility of OA/DMSA ligand exchange reaction. Hence, we designed a novel protocol accessing monodisperse IONPs with controlled and reproducible DMSA-surrounding shell (n=4). To assess their biomedical potential, we PEGylated (via EDC chemistry) and labeled with a fluorophore (via 'click' chemistry) the treated DMSA-IONPs, in order to promote optical and magnetic resonance imaging (OI/MRI). As control, the same procedure was repeated using untreated DMSA-IONPs. Both set of particles were compared by confocal laser scanner microscopy (CLSM), demonstrating the superior properties of treated ones. In vivo, the treated DMSA-IONPs were able to accumulate in an orthotopic mice model of human breast cancer (n=4) by enhanced permeability and retention effect (EPR). As demonstration, a significant T<sub>2</sub> signal decrease (n=4) and optical tracking have been achieved. The results were confirmed by immunohistochemistry. In sum, we here present a protocol accessing a flexible and standardized nanoparticle-based platform with theranostic ability.



**Figure 1.** General Scheme

**Acknowledgements** M.F. acknowledges the financial support of MINECO and FEDER for research grant no. SAF2014-59118-JIN.

# Combining the Best of two Worlds: Protein-Polymer Coatings for Stimulated Phase Transfer of Nanoparticles

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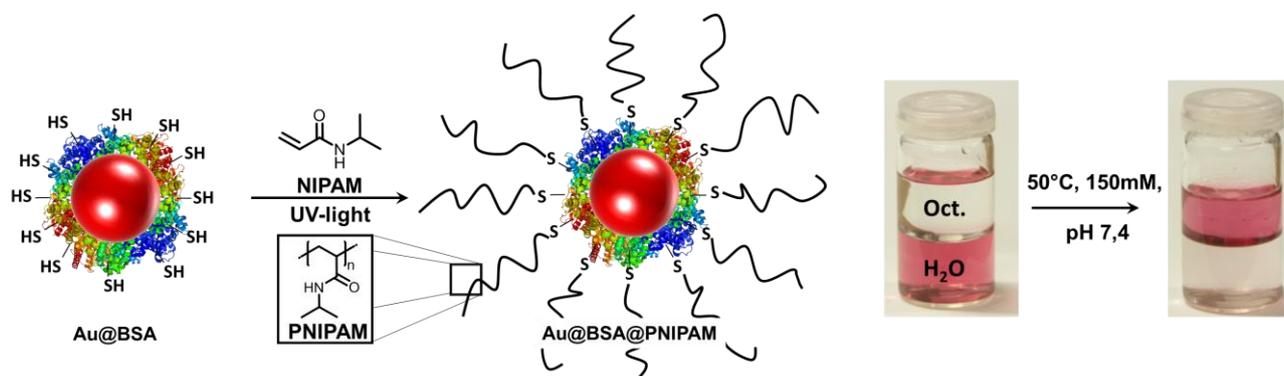
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Protein-coated gold nanoparticles (NPs) are essentially ideal candidates for *in vivo* testing as they exhibit high colloidal stability at large pH ranges, at high ionic strength and at high concentrations.[1,2] Furthermore, their protein shell circumvents an unspecific protein adsorption during biomedical applications. The charge of the NPs can be tailored through the choice of the protein and the environmental conditions. However, it is not yet possible to tune their hydrophobicity, as the particles aggregate at the isoelectrical point.[1]

Therefore, we applied a simple modification of the particles without a catalyst and without pre-modification of the protein coating. Protein-initiated thiol-ene photopolymerization of *N*-isopropylacrylamide (NIPAM) was used for the generation of the hybrid NPs. The switchable phase transition behavior of PNIPAM at 32°C generates multiresponsive (pH, ionic strength, temperature) NPs, which can then undergo a stimulated phase transfer from water to octanol. Such a transfer displays an increase of hydrophobicity, which is a common indicator for the NPs' potential in biomedical applications.[3]



**Figure 1** Synthesis of Au@BSA-PNIPAM NPs by thiol-ene photopolymerization of *N*-isopropylacrylamide (NIPAM) and the stimulated phase transfer from water to octanol under physiological conditions.

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# Hybrid pH-Responsive Au@p4VP Microgels as Platform for Selective SERS Analysis

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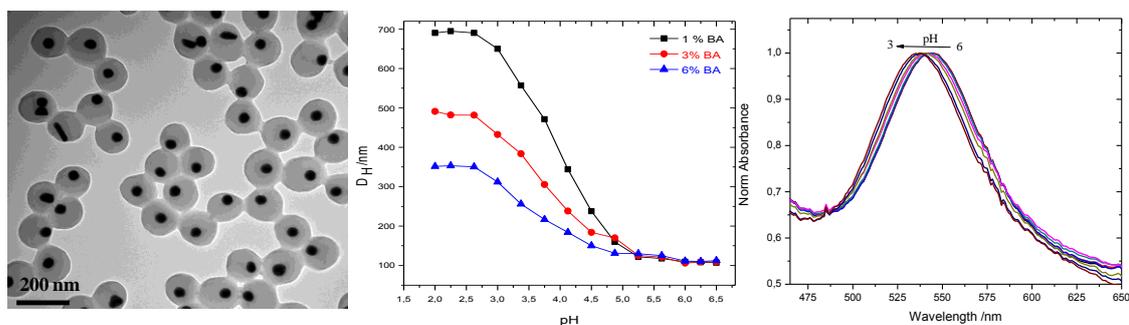
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We present the synthesis of a pH-responsive core@shell hybrid microgel. This colloidal system is formed by a 55 nm Au core individually covered by a polymeric pH-sensitive shell of poly(4-vinylpyridine), that we denote as Au@p4VP. Initially, we control the microgel thickness from 51 to 10 nm, and we confirm the pH-responsive capability of Au@p4VP by DLS measurements, showing a swelling degree, which depends on the pH of the media and the crosslinker density within the polymer network. We also prove the hybrid structure by plotting the UV-vis spectra at different pH values, showing a surface plasmon band displacement in function of pH. Thus, at acidic pH the microgel swells due to the electrostatic repulsion created into the polymer matrix, while at high pH, the microgel structure collapses because of the reduction in the electrostatic repulsion and the increment of the hydrophobic interactions. This capability is exploited to introduce doxorubicin molecules into the microgel network which are detected by surface-enhanced Raman spectroscopy (SERS). After increasing the pH of the solution, the captured molecules are brought in close proximity to the surface of the metallic core, enhancing its detection by SERS.



**Figure 1.** TEM images of the Au@p4VP system (left), DLS measurement at different crosslinking densities (middle), and UV-vis spectra at several pH values (right).

**Acknowledgements** The financial support of this work was supplied by the Spanish MINECO grants CTQ2013-48418P and MAT2013-45168-R

# Hyperuniformity of bidisperse particle mixtures

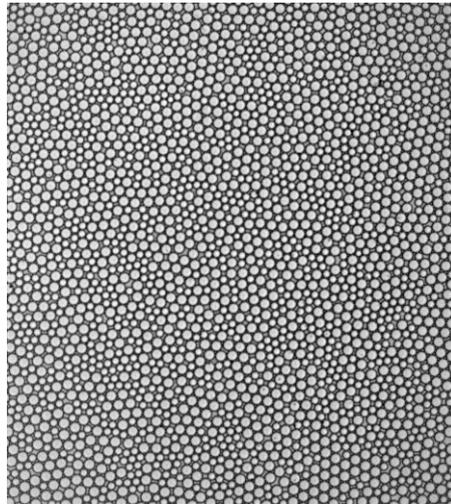
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Hyperuniform materials [1], being disordered systems with suppressed long-scale fluctuations have been demonstrated to exhibit potential applications for disordered photonic materials production [2]. In our project we study a jammed packing of oil droplets in water which is a suitable model of Maximally Random Jammed systems. The droplets are produced in a PDMS microfluidic chip and directly assembled in a microfluidic channel. The pseudo-2D (a monolayer of droplets) system is investigated. By varying the fluid pressures we manage to sharply control the droplet production and thereby govern the structural properties of the obtained material. Various types of defects inducing density fluctuations can be tuned and at appropriate experimental conditions droplets self-organize in hyperuniform patterns. Our electromagnetic simulations also show that the obtained material can be transparent while staying optically dense.



**Figure 1** Bidisperse emulsion of droplet. This hyperuniform material exhibit vanishing density fluctuation at longscale

**Acknowledgements** The Microflusa project receives funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No. 664823

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# Platinum nanoparticles from the recycling of spent screen-printed electrodes to be used as hydrogen peroxide sensors

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Screen-printing is nowadays a widely used technology for large-scale fabrication of disposable sensors and biosensors at low cost, with numerous analytical applications in biomedical, pharmaceutical, food, industrial and environmental analyses. However, an important consequence of this is a serious problem of accumulation of solid waste containing hazardous but precious metals like platinum which should be appropriately managed and treated to ensure a high level of environmental and public health protection.

This work presents, for the first time, a procedure to recycle platinum from waste screen-printed platinum electrodes (SPPtEs) using HNO<sub>3</sub>:HCl (1:3, v/v), namely aqua regia, as the leaching solution. Platinum from platinum ink was recovered by chemical and electrochemical techniques, and was then used in electrochemical sensor manufacturing. Platinum nanoparticles (PtNPs) were electrodeposited onto the surface of screen-printed carbon electrodes (PtNPs@SPCEs) directly from the acidic leaching solution, and were successfully applied as a hydrogen peroxide sensor, with similar results to those obtained with PtNPs from standard hexachloroplatinic acid solutions. PtNPs were characterized by SEM and X-ray diffraction analyses. With very small quantities of deposited platinum (μg), the reached sensitivity of the best herein obtained PtNPs@SPCEs (at -0.4 V for 900 s) was 687.3 nA cm<sup>-2</sup> μM<sup>-1</sup> and the limit of detection was 1.9 μM (based on a signal-to-noise ratio equal to 3). In this particular sensor, the PtNPs were snowflake-shaped particles. The sensitivity towards H<sub>2</sub>O<sub>2</sub> was improved ~360 times compared to commercial SPCEs, and ~7 times compared to commercial SPPtEs. These results show that the electrodeposition of recycled Pt from waste SPPtEs onto the surface of SPCEs is a promising low-cost tool for the fabrication of different sensor approaches. A two-fold environmental benefit is achieved with this process: the amount of solid waste generated by using disposable electrodes in laboratories is reduced, and it allows a precious metal like platinum to be recovered at low cost.

**Acknowledgements** The financial support of the Spanish Ministry of Economy and Competitiveness (MINECO, <http://www.mineco.gob.es/portal/site/mineco/idi>), Projects No. BFU2013-44095-P and BFU2016-75609-P (cofounded with FEDER funds, EU) is acknowledged. BGM is a post-doctoral research fellow of the Youth Employment Initiative (JCCM, Spain, cofounded with ESF funds, EU).

# Gold Nanoparticles Insertion Into Organized Block-Copolymer Films

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In order to fabricate nanocomposites with new optical functionalities, we study the formation and the insertion of gold nanoparticles (AuNPs) inside a self-assembled diblock copolymer polystyrene-*block*-poly(vinylpyridine) (PS-*b*-PVP) diblock copolymer.

We report here two ways of inserting AuNPs inside a copolymer film. The first method uses the formation of AuNPs by sonication and their introduction in ordered films of PS-*b*-PVP. The spin-coating of the PS-*b*-PVP solution in an appropriate solvent on a substrate casts a film of oriented cylinders, with the PVP-cylinders perpendicular to a substrate. The mixture of gold chloride (AuCl<sub>3</sub>) with the PS-*b*-PVP solution and a following ultra-sound treatment before casting the film provide small, spherical AuNPs (2-3 nm in size) [1] located, after deposition, inside the PVP cylinders. No major perturbation of the cylinder organization was observed. Larger AuNPs (up to 8 nm) were also obtained by a seeded-growth method, through the addition of gold salt to the AuNPs containing-solution followed by sonication for successive times. These AuNPs locate inside the cylinders after casting the film and exhibit a plasmon resonance.

The second process is the formation of AuNPs directly inside the copolymer film by a chemical reduction [2]. The PS-*b*-PVP film is cast and organized as perpendicular cylinders. The PS matrix surrounding the cylinders is then cross-linked by UV-irradiation in order to freeze the organization. The immersion in a gold salt (HAuCl<sub>4</sub>) solution followed by a chemical reduction with a sodium borohydride (NaBH<sub>4</sub>) aqueous solution leads to the formation of AuNPs (with a diameter of 7 nm) inside the cylinders. The AuNP growth by further reduction cycles could be operated with ascorbic acid (AA) impregnation.

Other ways to achieve this same goal were also studied, through AuNP functionalization [3] or with insertion of AuNPs into porous membranes. The structural (by Atomic Force Microscopy, Transmission Electron Microscopy and Grazing-Incidence Small-Angle X-Ray Scattering) and optical (by Spectroscopic Ellipsometry) studies validate these processes for the AuNP insertion in patterned films, which provide new plasmonic nanocomposites.

We acknowledge the support of CEA, the Région Aquitaine, and the AMADEus LabEX (ANR-10-LABX-0042-AMADEUS/ANR-10-IDEX-0003-02).



**Figure 1** Illustration of the formation and insertion of AuNPs in patterned films of perpendicular cylinders via sonication method (I) and in situ chemical reduction (II).

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# Investigating the Static and Dynamic Behavior of Microemulsion - Polyelectrolyte Complexes

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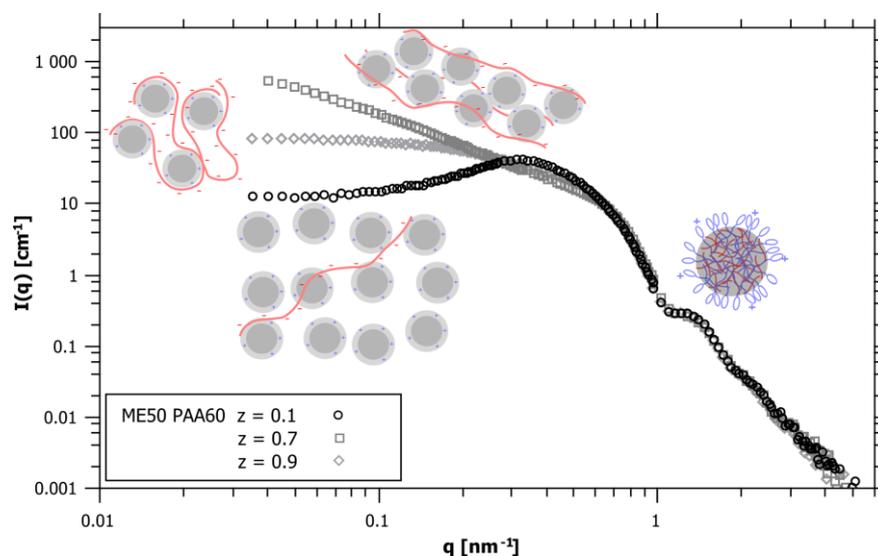
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By mixing polyelectrolytes (PE) with oppositely charged colloids one can modify the structural and rheological properties of the system. For the case of surfactants that leads to surfactant-polyelectrolyte complexes (SPECs). The contained micelles are often used as carriers for drug molecules, pollutants, reactants and similar substances that otherwise couldn't be dispersed in the solvent. It is therefore of high interest to investigate the behavior of 'loaded carriers', which often behave quite differently to the respective (empty) micelles.

Accordingly we studied the interactions of positively charged O/W microemulsion (ME) droplets that already contain a substantial load of solubilized molecules with negatively charged polyelectrolytes. In our experiments we varied size and charge density of the droplets, and the type and Mw of the PE. Based on a thorough determination of the phase behavior and employing small-angle neutron scattering (SANS; see Fig. 1) it was possible to obtain a detailed characterization of the formed complexes in terms of size, shape and composition.

The interconnected nature of the droplet aggregates was studied using pulsed field gradient NMR (PFG-NMR), neutron spin-echo (NSE) and fluorescence correlation spectroscopy (FCS). This way, it was possible to investigate the diffusional behavior of free microemulsion droplets as well as of droplets immobilized in the complexes and gain insights into the dynamic aspect of such mixed colloidal systems.

In our experiments we obtained a comprehensive picture of the formed complexes and how their detailed structure depends on their molecular composition, as well as the interactions prevailing here. These aggregates serve as a model system for complexes with a high solubilization capacity that could find potential applications in formulations which contain a large amount of oil or hydrophobic agents with controlled viscosity and internal mobility, both required for optimized delivery.



**Figure 1:** SANS curves  $I(q)$  and corresponding structures of microemulsion – polyacrylate complexes for three different charge ratios  $z = [-]/([+]+[-])$ .

# Nonionic cleavable monomeric and dimeric surfactant: effect of the temperature on the degradation

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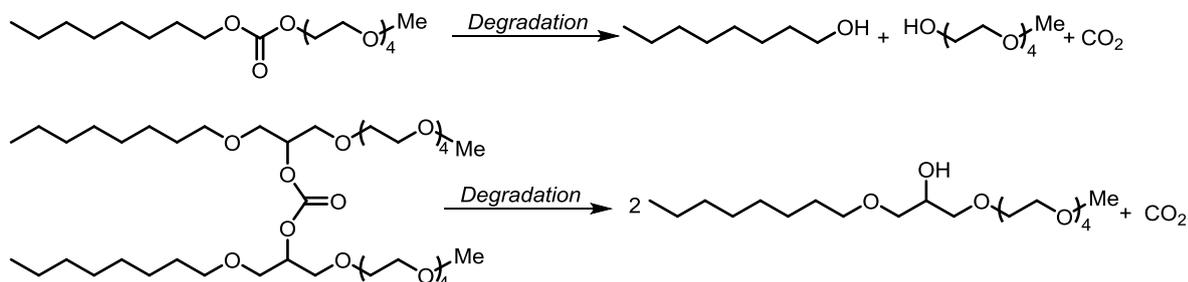
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The possibility of introducing a cleavable bond in the surfactant structure has raised considerable attention through the years and most of the work carried out has been dedicated to studies of degradation paths and mechanisms.

Here, our focus has been on nonionic carbonate-based surfactants, either monomeric or dimeric (gemini type). The monomeric carbonate surfactant with a C8 hydrophobic tail and with tetra(ethylene glycol)monomethyl ether on the other side of the carbonate linkage was prepared by reacting n-octylchloroformate with tetra(ethylene glycol) monomethyl ether at low temperature. The dimeric surfactant was prepared in a two-step approach; first a single tail surfactant having glycerol as a linker between the polar headgroup and the hydrophobic tail was prepared. In a second step, the gemini surfactant was synthesized by taking advantage of the free hydroxyl group of the glycerol moiety to form a carbonate bridge between two moieties (see figure below).

With a balance of 4 oxyethylene units in the headgroup for 8 carbons in the hydrophobic tail, the surfactants exhibited cloud points close to room temperature. The physical chemical properties were therefore investigated at 15°C, by tensiometry.



**Figure 1** Degradation reaction of the carbonate-based surfactants; top monomeric, bottom dimeric.

The degradation of the surfactants was monitored at different pH values and at 15°C and 30°C by tensiometry and by NMR. As expected, the hydrolysis was fast under alkaline conditions. The position of the carbonate group played a role in the degradation and we could demonstrate that having the carbonate unit as spacer in the gemini surfactant led to lower rate of hydrolysis as compared to when the carbonate was placed between the hydrophobic tail and the polar headgroup of the monomeric surfactant. This was counter to our expectations. The temperature was also found to be crucial and played an unexpected role: the rate of degradation was much faster at 15°C than at 30°C. This is explained as an effect of decreased solubility of the nonionic amphiphile with increasing temperature, which, in turn, is due to reduced hydration of the oligo(ethylene glycol) chain at higher temperature.

**Acknowledgements** This work has received funding from the European Union's Horizon 2020 research and innovation programme under the NanoRestArt project.

# COMBINATION OF WATER-IMMISCIBLE AND WATER-MISCIBLE SOLVENTS IN DEXAMETHASONE-LOADED MICROSPHERES PLGA ELABORATION

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Dexamethasone (Dx) is a steroidal anti-inflammatory drug extensively used in the treatment of chronic diseases of the posterior segment (1). Drug delivery systems (DDS) have risen as interesting alternative to repeated intravitreal injections in the treatment of chronic retinal diseases, as they are able to release the loaded active compound even for months. Poly lactic-co-glycolic acid (PLGA) microspheres (MSs) are currently one of the most widely studied systems for this purpose(2). Among the different technological approaches to prepare PLGA MSs, the most employed are those involving the preparation of an O/W emulsion followed by an organic solvent extraction/evaporation step. Within elaboration process, the diffusion rate of the organic solvent into the external aqueous phase is crucial to the PLGA precipitation conditioning properties of the final MSs formulation such as encapsulation efficiency among others. The aim of the present work was to evaluate the partial substitution of the water-immiscible solvent generally used (methylene chloride, MC) by a water-miscible co-solvent (acetonitrile, ACN) during Dx-loaded MSs elaboration.

Dx-loaded MSs were prepared by the O/W emulsion solvent extraction-evaporation technique using a combination of MC:ACN as solvents of the inner phase. Two different ratios of the solvents mixture (2.5:1.5 and 1:1) were tested. Three types of PLGA polymer (PLGA 50:50 16.000 g/mol; PLGA 50:50 35.000 g/mol and PLGA 85:15 87.000 g/mol) were evaluated.

The production yields for all formulations were higher than 44% in all cases presenting unimodal distribution within the most adequate size fraction for intravitreal injection (38-20  $\mu\text{m}$ ). The type of polymer and the organic solvent composition influenced the surface roughness being smaller for PLGA 85:15 and MC:ACN (2.5:1.5) respectively. MSs formulations prepared with MC:ACN (1:1) presented encapsulation efficiencies slightly increased, being over than 60% in all cases. Concerning the *In vitro* release profiles, the composition of the inner phase did seem to influence the Dx release profile in some formulations (Table 1).

Table 1. Influence of the organic mixture of the inner phase in the Dx release profile (kinetic release profile and percentage of Dx released at 40 days).

	MC:ACN (2.5:1.5)	MC:ACN (1:1)
PLGA 50:50 (16,000 g/mol)	Zero-order kinetic Day 42 (~80%Dx released)	Zero-order kinetic Day 42 (~80%Dx released)
PLGA 50:50 (35,000 g/mol)	Biphasic profile Day 42 (30% Dx released)	Zero-order kinetic Day 42 (40% Dx released)
PLGA 85:15 (87,000 g/mol)	Biphasic profile Day 42 (10% Dx released)	Zero-order kinetic Day 42 (35% Dx released)

We can conclude that the rapid diffusion of the water-miscible solvent from the organic phase during microencapsulation process achieved a high Dx entrapment into the polymeric matrix and a sustained release profile. Moreover, the mixture of MC:ACN (1:1) seems to promote a zero-order kinetic in all cases.

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# Protein-polyelectrolyte complexes to improve the bioactivity of proteins in layer-by-layer assemblies

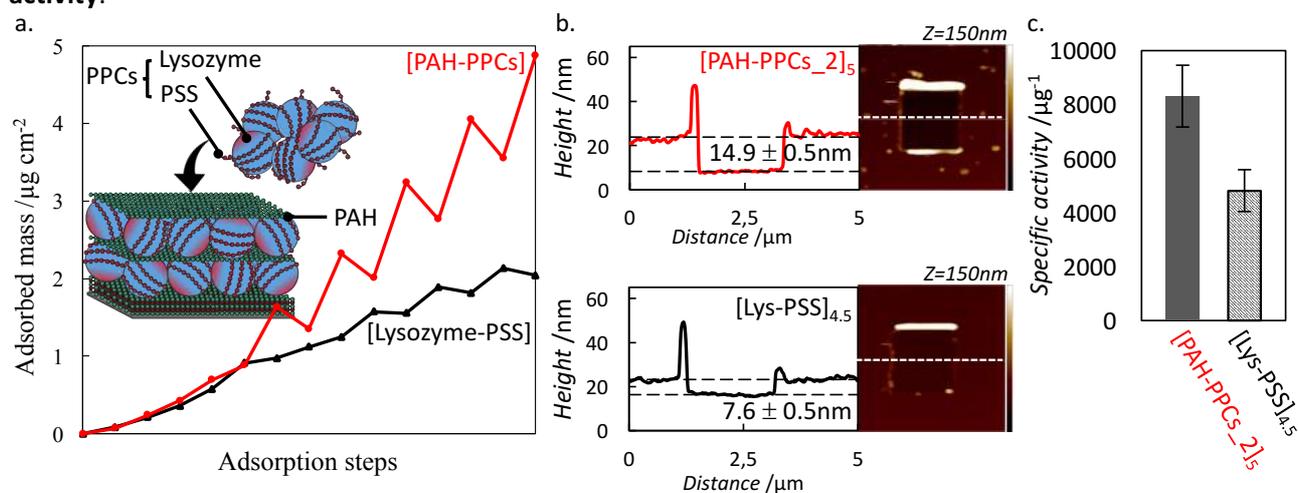
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The ability to **control the immobilization of proteins** at interfaces is a major challenge for many applications in biomedical science and biotechnology. We propose a reaction-free method for protein immobilization based on **protein-polyelectrolyte complexation (PPCs)** and the subsequent integration of these complexes in multilayers by the layer-by-layer method (LbL). Specifically, relying on quartz-crystal microbalance (QCM) combined with spectroscopic techniques and scanning probe microscopy, it was shown that lysozyme can be effectively immobilized in multilayers using such an approach (Figure 1 a,b). The biological activity of lysozyme is not only maintained, but its specific activity is also higher for multilayers integrating PPCs (Figure 1 c). This new finding offers a **potential range of applications** with respect to **proteins that cannot yet be immobilized within LbL assemblies while keeping their enzymatic activity**.



**Figure 1** a. Scheme of the layer-by-layer assembly of protein-polyelectrolyte complexes (PPCs) with polyallylamine hydrochloride (PAH). Adsorbed mass measured by QCM after adsorption of a cushion of two PAH-polystyrene sulfonate (PSS) bilayers followed by either [Lys-PSS<sub>n</sub>]<sub>5</sub> or PAH-PPCs with (-)/(+net)=2 (PPCs<sub>2</sub>) at pH 7.5 in HEPES buffer. b. Topographic images of glass surfaces coated with a [PAH-PSS<sub>n</sub>]<sub>2</sub> cushion followed by [Lys-PSS<sub>n</sub>]<sub>4.5</sub> or [PAH-PPCs<sub>2</sub>]<sub>5</sub> obtained by atomic force microscopy (AFM) in contact mode after scratching a  $2 \times 2 \mu\text{m}^2$  central area at high applied load, and cross-sections corresponding to the broken line on topographic images. c. Lysozyme specific enzymatic activity measured for [PAH-PPCs<sub>2</sub>]<sub>5</sub> and [Lys-PSS<sub>n</sub>]<sub>5</sub>. Enzymatic activity was measured through the release of fluorescent MeU following (GlcNAc)<sub>3</sub>-MeU glycosidic bond hydrolysis. Protein amount was assessed by a bicinchoninic assay.

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# Molecular assembly in block copolymer-surfactant nanoparticle dispersions: Information on dissociated species from NMR diffusometry.

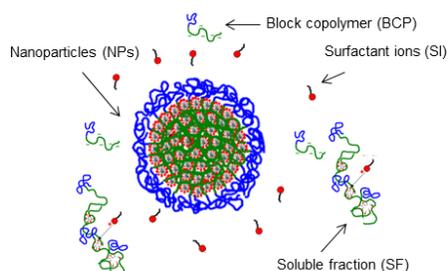
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We have developed a procedure to reproducibly prepare water-dispersible core-shell block copolymer-surfactant nanoparticles with liquid crystalline core structures. The particles are made from symmetric (42-42) or asymmetric (69-422) poly(acrylic acid-*b*-acrylamide) block copolymers, where the acrylic acid block has been neutralized by cationic dodecyl- and hexadecyltrimethylammonium hydroxide surfactants. The core of a dispersed particle contains densely packed, ordered surfactant ion aggregates interspersed with the anionic blocks of the copolymer, while the neutral hydrophilic blocks are enriched at the particle surface. The nanoparticles have an average radius of ca 120 nm and possess a negative surface charge. The nanoparticle dispersions are kinetically stable for several months, as evidenced by monitoring their average size and zeta potentials with time<sup>1</sup>. We have now employed Pulse Gradient Spin Echo NMR (PGSE-NMR)<sup>2</sup> to study the dynamics and organization of both surfactant ions and block copolymers in the nanoparticles dispersions, by means of their self-diffusion coefficients ( $D$ ). It is possible to prepare, by centrifugation, systems that contained one phase concentrated in nanoparticles separated from a clear dilute phase.  $D$  values for both species in the two phases indicated that the dilute phase contained a "soluble fraction" of small aggregates of surfactant ions and anionic-neutral block copolymers, diffusing together at least an order of magnitude more rapidly than the nanoparticles collected in the concentrated phase. The fraction of block copolymer found in the dilute phase was nearly constant, independently of the overall concentration of the dispersions. In both phases, the surfactant degree of dissociation was small (less than 1%) and the block copolymer/surfactant ratio was quite similar. Additional studies employing samples with particles labeled with a hydrophobic probe and light scattering studies confirmed the presence of a fraction of small aggregates of surfactant ions and block copolymers coexisting with the nanoparticles (Fig. 1). We will present the detailed results obtained for the various investigated systems and discuss the molecular assembly and behavior of the different species dissociated from the dispersed block copolymer-surfactant nanoparticles.



**Figure 1** – Molecular species dissociated from block copolymer-surfactant dispersed nanoparticles.

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# Prediction of Transport Properties of Hybrid Bilayer Ion-Exchange Membranes

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American cation-exchange perfluorinated membrane Nafion-117® (DuPont de Nemours) and its Russian analogue MF-4SC (JSC Plastpolymer) are among the mostly used as separators in fuel cells, electrolyzers, electrodialyzers, sensors and investigated ion-exchange materials. Surface and spatial modification of ion-exchange membranes by incorporation of different inorganic dopants allows to change their characteristics: stability and structural properties as well as ion and molecular transport [1]. This poses the priority problem of a reliable characterization of the newly created hybrid nanocomposites membranes. Here we propose to solve this problem for bilayer hybrid membranes, based on a theoretical examination of the electrodiffusion transport and our own experimental data for monolayer membranes. As a dopant, halloysite and platinum nanoparticles were used. Halloysite nanotubes of 2% by weight were added to one of the membrane layers during its synthesis by casting method. Bilayer membranes consisting of a thick layer of a pure perfluorinated membrane MF-4SC and a thinner layer of the same membrane modified by halloysite nanotubes, functionalized with platinum nanoparticles were investigated. The study of the transport characteristics of perfluorinated membranes after their modification showed that the diffusion permeability of hybrid membranes is somewhat lower in comparison with the initial (pure) membrane. The integral coefficient of diffusion permeability of the modified membrane decreases by 50-55%. This suggests that under the operating conditions of the fuel cell the crossover through the modified membranes will be lower. The electric conductivity of membranes increases after modification. The greatest effect of increasing the electric conductivity (by about 30%) was noted for a sample modified with halloysite and Pt. Since the observed changes in the structural characteristics cannot cause such an increase in the conductivity of the samples, the possible cause of this effect can be the contribution of the electronic conductivity of the metal. Thus, the modification of the perfluorinated membrane by the halloysite nanotubes with platinum nanoparticles deposited on their outer surface does not lead to a noticeable change in the structure of the membranes and does not worsen their transport properties.

One of the samples revealed a weak asymmetry of diffusion permeability and the current-voltage characteristics. Using the physicochemical parameters of monolayer membranes obtained earlier, the dependence of the diffusion permeability of the bilayer composite on the electrolyte concentration is described with satisfactory accuracy. The numbers of water transport and the selectivity of hybrid membranes, as well as their power characteristics in the membrane-electrode block of the fuel cell, were studied. The introduction of halloysite leads to a decrease in both parameters, and the subsequent addition of platinum compensates for the negative effect of halloysite adding: the maximum specific power becomes higher than for the original (pure) membrane, the range of operating current densities increases. This makes it possible to predict the effective use of hybrid membranes based on MF-4SC and halloysite nanotubes with platinum nanoparticles, not only as separating diaphragms in fuel cells and electromembrane devices, but also as promising catalytic systems.

**Acknowledgements** This study was supported by the Ministry of Education and Science of the Russian Federation (Grant No 14.Z50.31.0035).

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# Crystallization in confinement

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The crystallization of water, various polymers and liquid crystals in self-ordered nanoporous alumina (AAO) was studied as a function of pore size, pore surface functionality, molecular weight and cooling/heating rate by differential scanning calorimetry (DSC), wide-angle X-ray diffraction and dielectric spectroscopy. As polymers we analysed: polyethylene oxide (PEO), highly isotactic polypropylene, poly( $\epsilon$ -caprolactone) (PCL) and a series of poly(ethylene oxide)-*b*-poly( $\epsilon$ -caprolactone) (PEO-*b*-PCL) diblock copolymers. In small pores the liquids/melts crystallize predominantly by homogeneous nucleation. In contrast, in bulk or large pores crystals are formed by heterogeneous nucleation. Water crystallizes in a cubic phase rather than the hexagonal when confined in pores smaller than 1  $\mu\text{m}^3$ . These results highlight an important function of interfaces: Confining crystallization to defined compartments.

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# Shear induced network orientation of capillary suspensions

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The addition of small amounts of an immiscible secondary fluid to a suspension can dramatically change the rheological behavior of the suspension by inducing gelation or reinforcing a weak network into a strong network [1]. This transition is caused by strong attractive capillary force between the particles and two fluids producing a sample-spanning network [2]. Capillary suspensions exist in two states: a pendular state when the secondary fluid preferentially wets the particles, and a capillary state when the bulk fluid is preferentially wetting.

These capillary suspension networks demonstrate a negative normal stress difference, which indicates a re-orientation of the flocs into the vorticity direction during shearing. Typically, systems with such negative normal stress differences either have high volume concentrations ( $\phi \sim 58\%$ ) and are shear thinning, or are shear thickening with very low particle concentrations ( $\phi \sim 0.09\%$ ) [3, 4]. In contrast, the capillary suspensions we report here have a 25% solid concentration and are shear thinning. In the pendular state, the system undergoes a transition from a positive normal stress difference at the high shear rates to a negative one at the low shear rates. Analogue experiments also have been run for the capillary state. The system showed only a negative normal stress difference. These results, therefore, might be indicative of more rigid flocs in the pendular state that are able to undergo solid-body rotation to reorientate under shear in the pendular state, and forming more networks due to more droplets breakup at higher shear rates in the capillary state. Furthermore, we compare the rheological properties and images from confocal microscopy during shearing to gain insight into the network microstructure.

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# Kinetic and Random graph theory based model for pH drop dependent material properties in an acid triggered supramolecular hydrogel

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pH triggered supramolecular hydrogels are a recent development in the field of soft materials and are touted to be possible alternatives to polymeric gels for biomedical applications [1]. In recent years, the effect pH triggering on the mechanical properties [2] and morphology [3] of supramolecular gels have been probed using hydrolyzable lactones and anhydrides [4]. The view is that kinetics of gel self-assembly along with supersaturation accounts for observed mechanical properties in the case of a model hydrogelator. However, the role of kinetics on microstructure is yet to be fully explained and explored. Network growth models have recently been adapted to reconcile microstructure based on mechanical properties [5-7] in the case of organogelators in organic solvents. In our contribution we evaluated the validity of these models for a chosen acid triggered hydrogelator (DBC) (Fig.1). We observed that Avrami model (Fig.1A) accounts for changes in network fractal dimensions better when compared against confocal microscopy images (Fig.1E) in the explored concentrations of gelator and triggering agent (GDL). In addition, we developed a kinetic model based on solubility and combined it with a random graph theory model [8] to predict gel point ( $t_{gel}$ ) that correlates well with rheology measurements (Fig. 1D). This is a new attempt towards kinetic modelling in pH triggered low molecular weight gelators to predict quantities that are needed to optimize formulations.

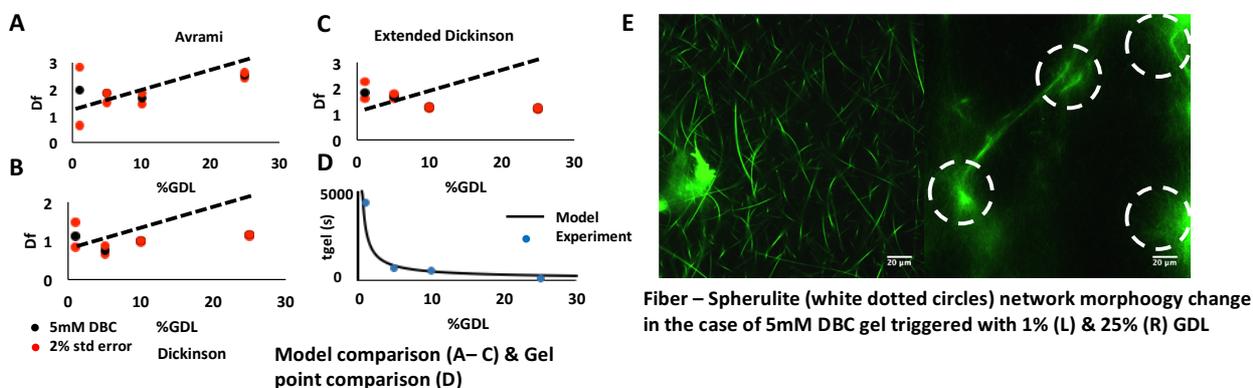


Fig 1. Model predicted  $D_f$  (A-C), gel point (D); Confocal micrograph showing morphology change (E)

**Acknowledgements** This PhD project is funded by NanoNextNL Programme, Project 07A.11

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# Polyelectrolyte complexes and multilayers: ion-specific effects and overcharging

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The similarities between processes of polyelectrolyte complex (PEC) and multilayer (PEM) formation have been recognized for quite some time. On the other hand, the most important question regarding the apparently different outcomes of interpolyelectrolyte neutralization in solution and at the surface (*i.e.* overcharging) has not been fully answered yet [1]. In order to investigate the correlation between interpolyelectrolyte neutralization in solution and at the surface, we explored systems containing two oppositely charged synthetic polyelectrolytes by means of dynamic light scattering, electrophoretic light scattering, isothermal microcalorimetry and quartz-crystal microbalance with dissipation monitoring. As cationic polyelectrolytes we used poly(diallyldimethylammonium chloride), poly(allylamine hydrochloride) and poly(N-ethyl-4-vinylpyridinium bromide) and as anionic we used poly(sodium 4-styrene sulfonate). We have managed to observe the overcharging phenomenon in solution directly, by changing the experimental procedure [2].

Apart from the phenomenon of overcharging, the counterion-specific effects, especially counteranion-specific, are of great interest in the field of polyelectrolyte chemistry, however the detailed investigations of related phenomena were mostly performed in the case of multilayers. Even though multilayers offer more promising application possibilities, the studies of interpolyelectrolyte neutralization in solution are often much simpler and faster to perform [3,4]. One of our goals was to explore in which measure the results of investigation regarding the influence of counterion type and concentration on the polyelectrolyte complexation in solution could be used for predicting the outcome of interpolyelectrolyte neutralization at the surface, as well as to provide information about long-term stability of these systems.

**Acknowledgements** The research was financially supported by Croatian Science Foundation under the project SAQUINT (IP-2014-09-6972).

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# Electrolyte-induced Attraction of Sterically Stabilised PMMA Particles in a Low Dielectric Solvent

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The technique of blinking optical tweezers (BOT) has been invaluable in measuring inter-particle forces in colloidal systems and provides a means of testing the validity of theories such as the classic DLVO. One system for which we believe DLVO does not explain observed behaviour is that of micron-sized poly(methyl methacrylate) (PMMA) particles in the low dielectric solvent dodecane, at low electrolyte concentrations. Specifically, we have observed that addition of small amounts ( $\mu\text{M}$ ) of electrolyte results in PMMA aggregation, despite their strong electrostatic stability. The aggregates formed become larger and less linear as the electrolyte concentration is increased, suggesting a weakening of the long-range repulsion, and appearance of a short-range attraction. Therefore we seemingly have a case of like-charge attractions between PMMA particles in the presence of an electrolyte.

By using BOT and microscopy, we discuss the possibility that the origin of this attraction is a depletion interaction due to clustering of the electrolyte molecules in this poor quality solvent. With increasing electrolyte we simultaneously decrease the Debye length, weakening the electrostatic stability, and strengthen the depletion attraction as the clusters, or Bjerrum pairs [1], enlarge to the point of insolubility at electrolyte concentrations of just  $500 \mu\text{M}$ .

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# The role of directional interactions in the designability of generalized heteropolymers

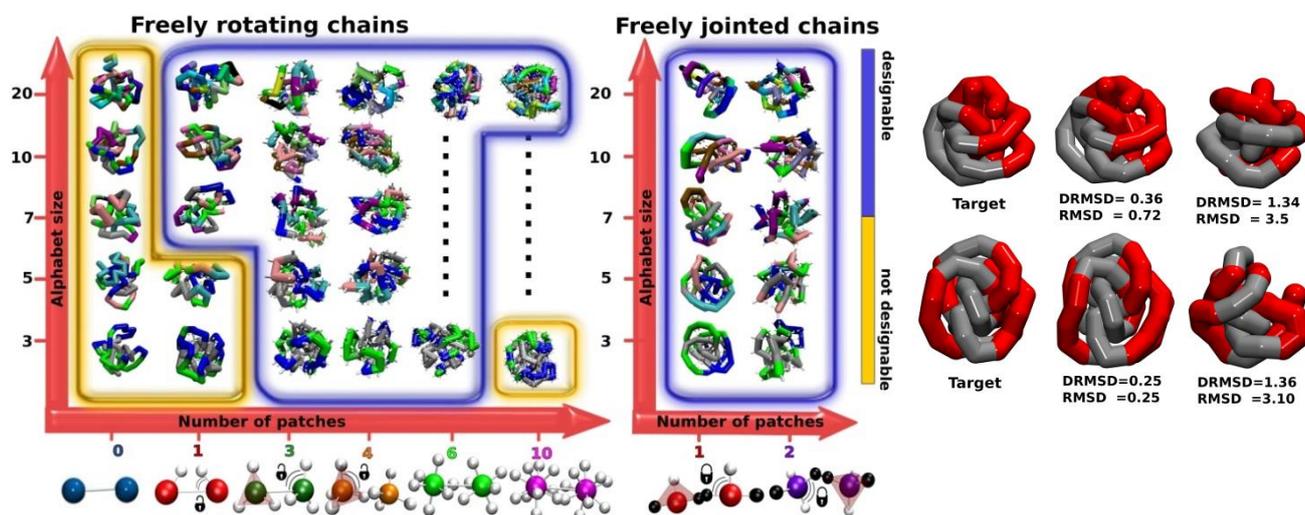
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Heteropolymers are important examples in material science of self-assembling systems. The technology for the synthesis and manipulation of such heteropolymers is already advanced, and it is nowadays possible to synthesize polymers made of up to 7 different monomers with complex pattern arrangements (e.g. block copolymers) [1,2]. However, it is still not possible to design heteropolymers with control over the single chain self-assembling properties comparable to what natural bio-polymers, such as DNA and proteins, can achieve. Here we introduce a criterion to discriminate between polymers that can be designed to adopt a predetermined structure from polymers that cannot, and show that this criterion is fulfilled by the addition of few directional interactions to the monomers of the chain. The criterion is based on the appearance of a particular peak in the radial distribution function that dominates over the random packing of the heteropolymer. We show that the presence of such a peak indicates that it exists at least one pattern that will drive the system to collapse towards a specific target structure. Moreover, we show that the peak is a universal feature of all designable heteropolymers, as it is dominating also the radial distribution function of natural proteins. The criterion that we present can be applied to engineer new types of self-assembling modular polymers that will open new applications for polymer-based materials science.



**Figure 1 a)** Designability diagram for different patches numbers and alphabet sizes. Within the yellow regions the heteropolymer is not designable, while the blue regions correspond to designable systems. For each case, the chosen target structure is shown. Bottom panel: schematic illustration of patchy polymers. White spheres indicate the patches located at the surface of the central monomer. For FRC (left) we consider from 0 (simple heteropolymer case) to 10 patches and 1 and 2 patches for FJC (right). **b)** Functionalized patchy polymer structures. Simulation snapshots showing the target structures with the desired functionalizations (left), the final folded structures obtained using our design procedure (centre) and examples of misfolded structures (right), the last two aligned with respect to the correspondent target structure. The values of DRMSD and RMSD are in units of the bead radius, that for proteins has been seen to correspond to approximately 2 Å, so in protein units the two folded structures would have a RMSD in the

range 0.5-1.4 Å and the two molten globule structures in the range 6-7 Å. Such functionalized polymers can, in turn, be used as Janus (one-patch) particles (top) or triblock Janus (two patches) particles (bottom).

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## ***In vitro* models to investigate the interaction between lipids and mucin: a micro-interferometry study**

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The accumulation of phosphatidylcholine (PC) in the intestinal mucus layer is crucial for the protection of colon epithelia from bacterial attack. It has been reported that the depletion of PC is a distinct feature of ulcerative colitis, a severe inflammation condition of the gastrointestinal tract [1]. Phosphatidylcholine (PC) and lyso-phosphatidylcholine (lyso-PC) share more than 90% of the phospholipids within the intestinal mucus [2], suggesting that PC/lyso-PC are either selectively transported or bound to this compartment. In a previous work we addressed the question how PC interacts with its binding glycoproteins, the mucins, which may establish the hydrophobic barrier against colonic microbiota. By systematic variation of net charges of the phospholipids' polar head, it was shown that dioleoylphosphatidylcholine (DOPC) has the strongest binding affinity with mucin, that cannot be explained within the electrostatic interactions between charged molecules [3].

In this study, an intestine surface *in vitro* model has been established by means of mucin supported membranes obtained by Biotinylation of mucin and subsequent deposition on NeutrAvidin-functionalised lipid bilayer. The validity of our *in vitro* model was proven by Western Blot and immunofluorescent assays. In a first instance, the vertical Brownian motion of cell-sized latex microparticles on mucin supported membranes was quantitatively measured with nanometer accuracy by means of a label free micro-interferometry technique, namely Reflective Interference Contrast Microscopy. The time evolution of the diffraction patterns was analysed making use of Derjaguin's approximation and Boltzmann's inverse work theorem to evaluate the particle confinement in a potential well [4]. By systematic variation of the latex particles' net charge it was shown that particles-mucin interaction follows the increasing electrostatic interaction. In a second instance, the same approach was used to quantitatively evaluate the lipid-mucin interactions by measuring the vertical Brownian motion of lipid-coated silica particles. In the latter case, by systematic variation of the net charges of the phospholipids' polar heads, it was shown that the lipid-mucin interaction does not follow the increasing electrostatic interaction.

**Acknowledgements** The research leading to these results has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° 606713.

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# Multi-scale approach to understand oil droplets collection by air bubbles in flotation: impact of salinity and water soluble polymer

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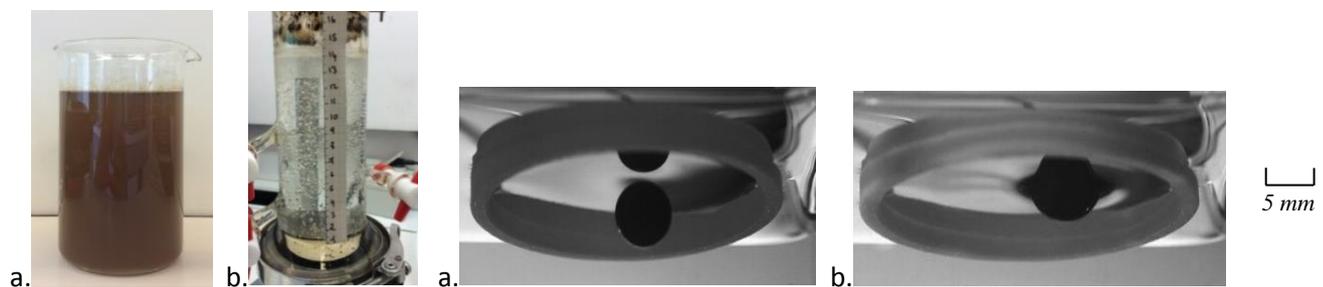
**Key words** : Flotation, droplet-bubble attachment, pseudoemulsion film dynamics, electrostatic repulsions.

Gas flotation is an efficient technique to remove oil droplets from oily produced waters. This method is mainly based on air bubble and oil droplet attachment and their combined rise. The three phase system oil/water/air is influenced by hydrodynamics, thermodynamics and interfacial phenomena. The creation of a stable link between an air bubble and oil droplets is governed by the pseudoemulsion film dynamics [1] and strongly influenced by physico-chemical parameters of the system and fluctuations caused by the environment [2].

By studying the impact of salinity at the macroscopic level using a lab flotation column (Figure 1), we emphasized the importance of electrostatic repulsions for oil droplets removal: flotation efficiency increases with the ionic strength. Indeed, the oil droplet surface charge results from the ionization of indigenous natural surfactants that depends on salinity. As a result, oil droplet zeta potential decreases when ionic strength increases, which favors their adhesion with bubbles.

To understand the mechanisms involved in the air/water/oil system for the droplet-bubble attachment, we characterized the stability of the pseudo-emulsion thin film thanks to a dedicated set up (Figure 2). We follow using a high speed camera the approach of a rising oil droplet toward an air/water interface and measure the drainage time of the pseudoemulsion film. To get a stable adhesion during the flotation process, the thin pseudoemulsion film has to be broken so that oil droplets can spread on the surface of bubbles. We observed that when increasing the salinity, the drainage time of the thin film is reduced. In fine there is a very good correlation between the microscopic thin film stability and the macroscopic flotation efficiency.

We studied also the impact of high molecular weight water soluble polymers on the drainage of the thin film and on the efficiency of flotation. Results show the strong influence of the rheological properties of the aqueous continuous phase when changing polymer concentration from a Newtonian behavior in the dilute regime to a shear thinning behavior in the semi-dilute regime.



**Figure 1:** Macroscopic scale:

- a. Produced water before flotation
- b. Clean water after flotation

**Figure 2:** Microscopic scale:

- a. Set up to observe oil droplet attachment on air/water surface
- b. Oil spreading

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# Building bridges driven by solvent transfer between droplets

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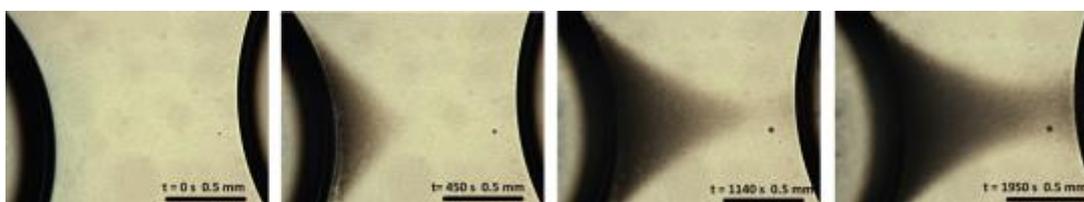
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Recently, tubes sprouting from water droplets injected in a system made of toluene, ethanol and silica nanoparticles has been reported [1]. The mechanism behind this growth is caused by the ethanol partitioning into the droplet, softening the interface, which gets covered with particles, enhancing the tube's mechanical strength.

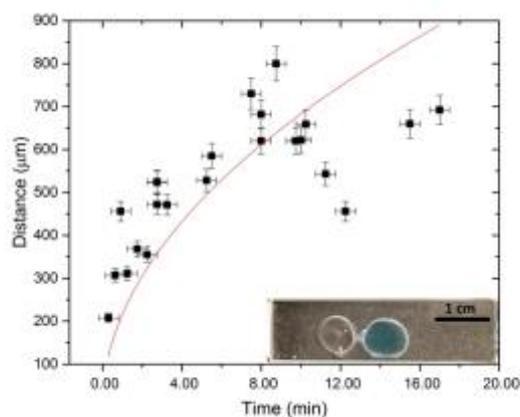
However, a new phenomenon has been discovered after injecting two droplets, one being pure distilled water and the other 50/50 % in volume water/ethanol. As shown in Figure 1, a structure develops in the water droplet growing towards the mixed one.

We have studied different features of these structures, such as the formation time versus the distance between droplets; the behavior is consistent with growth driven by composition differences in the continuous phase (see Figure 2). Elasticity and reversibility of the structure has also been observed when moving the droplets back and forth. Employing fluorescent silica particles, we have also confirmed that the particles are indeed covering the interface of the droplets. Interestingly, when zooming into the “bridge”, we find that it is made of tiny droplets. We suggest that spontaneous emulsification at the large droplet surface gives rise to the tiny droplets (*ca.* 5  $\mu\text{m}$ ), which are not covered by particles. These small droplets have limited mobility and coarsen slowly over time.

Spontaneous emulsification is attracting a lot of attention for applications as enhanced oil recovery, production of nanoparticles and food-grade emulsions, whereas particle-stabilized droplets are being widely employed in industry as emulsion stabilizers. Thus, this study is probing the relationship between these two topics of current interest



**Figure 1** Bridge formation from distilled pure water (left) towards mixed droplet (right) over a span of 32.5 minutes.



**Figure 2:** Time needed for the bridge to reach half the distance between droplets, fitted to a square-root like behavior. Inset is the experimental setup employed.

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# Structural characterization of model membranes containing DHA: the role of a unique molecule

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DocosaHexaenoic Acid (DHA) is the longest and most unsaturated fatty acid present in cell membranes, playing a pivotal role in the prevention of cardiovascular diseases and cancer and exerting a strong neuroprotective effect [1]. Among other hypotheses, mainly based on their radical-scavenging and anti-inflammatory action [2] it has been proposed that omega-3 fatty acids, to which DHA belongs, once converted to lipids could alter the structure of biological membranes, whose involvement in major biological processes, such as signaling and protein trafficking, is reported. However, how one molecule can be associated to many different beneficial effects is still unclear.

Lipid diversity regulates a wealth of biomembranes processes, because those molecules can tune the physicochemical characteristics of the lipid bilayer, such as elasticity, curvature, surface charge, hydration and the formation of domains by specific interactions involving the chemical structure, conformation and dynamics of the lipid head groups and acyl chains. For instance, it has been shown that certain lipids can promote nonlamellar phase formation, such as inverted hexagonal and cubic phases, as well as favor insertion of proteins into the membrane. These lipids, including sphingolipids and lysolipids, are defined non-bilayer lipids. Moreover, both theoretical and experimental data provide clear indications that, at least transiently, non-lamellar structural intermediates must exist *in vivo* [3].

With the aim to understand the functional role of DHA, we characterized at different scale levels, from micro-structure to overall morphology, different phospholipid systems containing this fatty acid. A variety of physico-chemical techniques such as Electron Spin Resonance (ESR) spectroscopy with the spin-labelling approach and Neutron Reflectivity (NR) were used to achieve our aims. Experimental results show that the presence of Omega-3 fatty acid produces significant changes in the biomembranes micro-structure, which reflects in a non-lamellar phase supporting the hypothesis that DHA behaves as a nonbilayer lipid, playing a key role as a morphological element to support the dynamic organization of cellular membrane systems.

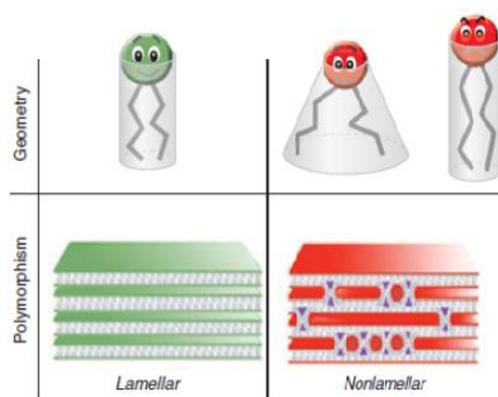


Figure: Cartoon scheme of the relation that occurs between geometry and polymorphism [4].

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# A combined *in-vitro/in-vivo* study to investigate the mucoadhesive mechanisms of cationic, anionic and uncharged emulsions in the mouth

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Mucoadhesive colloidal interactions are key in the interaction of oral dosage forms and food emulsions. To date there is limited understanding of the relative importance of the different colloidal interactions that govern mucoadhesion. Systematic *in vitro* & *in vivo* studies allowed us to understand which colloidal interactions were most important for determining the extent of emulsion mucoadhesion. The adsorbed mass of emulsions (stabilized by anionic, cationic and uncharged surfactants) remaining on surfaces coated with a salivary film was measured. Two techniques were used to measure this adsorption phenomena: A combined *in-vitro/ex-vivo* technique that observed the adsorption of emulsions onto a salivary film via Quartz Crystal Microbalance with Dissipation monitoring (QCMD) and Dual Polarisation Interferometry (DPI). Followed by human *in-vivo* measurements via a fluorescence spectroscopic probe to compare the mucoadhesive properties of emulsions in the mouth of humans.

Notable statistical differences in the mucoadhesive potential of different emulsions were observed and were primarily a consequence of the charge of the emulsifier used. Furthermore, *In vivo* measurements reflected the trends observed during *in vitro* measurements. This work therefore not only furthers our understanding of the key mechanisms of mucoadhesion in our mouths but also allows us to give an *a priori* prediction of whether an emulsion will adhere in the mouth simply based on knowledge of the emulsions formulation (e.g. ionic strength, pH, and emulsifier used). This information has the potential to help formulate 'healthier' foods and also improve the oral delivery systems used in the pharmaceutical industry.

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# Deswelling and deformation of microgels in concentrated packings

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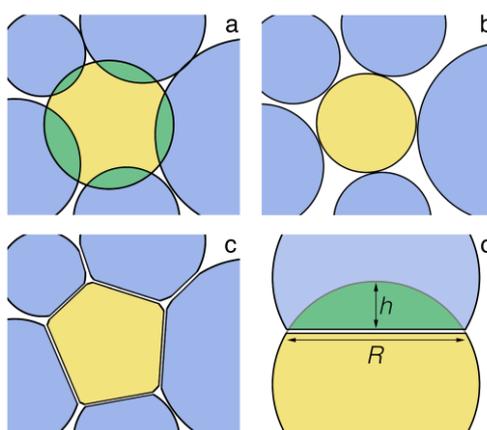
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Microgels are commonly used as a well-defined experimental model system to explore the phase behavior, dynamics and mechanics of soft particle suspensions [1]. Their softness, which entails both a low resistance to shape and to volume changes, has a large effect on the properties of dense suspensions of these particles. For example, they can be compressed to packing densities in excess of random close packing and their increase in viscosity as they approach the liquid-solid boundary shows significant deviations from the behavior of hard spheres [2,3].

Increasing the particle density of a suspension of microgel colloids above the point of random-close packing, must involve deformations of the particle to accommodate the increase in volume fraction. In contrast to the isotropic osmotic deswelling of soft particles, the contact of particles gives rise to a non-homogeneous pressure, raising the question if these deformations occur through homogeneous deswelling or by the formation of facets. Here we aim to answer this question by combining the imaging of individual microgels in dense packings with a relatively simple model to describe the balance between shape versus volume changes (Figure 1). We find a transition from shape changes at low pressures to volume changes at high pressures, which can be explained qualitatively with our model. Our results show that both types of deformation play a large role in highly concentrated microgel suspensions and thus must be taken into account to arrive at an accurate description of the structure, dynamics and mechanics of concentrated suspensions of soft spheres.



**Figure 1.** Osmotic compression of a microgel suspension leads to unphysical overlap between neighbors (a), which is resolved either by deswelling the particles (b) or through particle deformation in the form of contact facets (c). In the calculation of the energy of deformation by facet formation we use a Hertzian contact model in which the deformation is approximated by the overlap with penetration depth  $h$  leading to facets of size  $R$  (d).

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# Effect of nanoparticle size and shape on morphology and pore size distribution of conductive porous materials

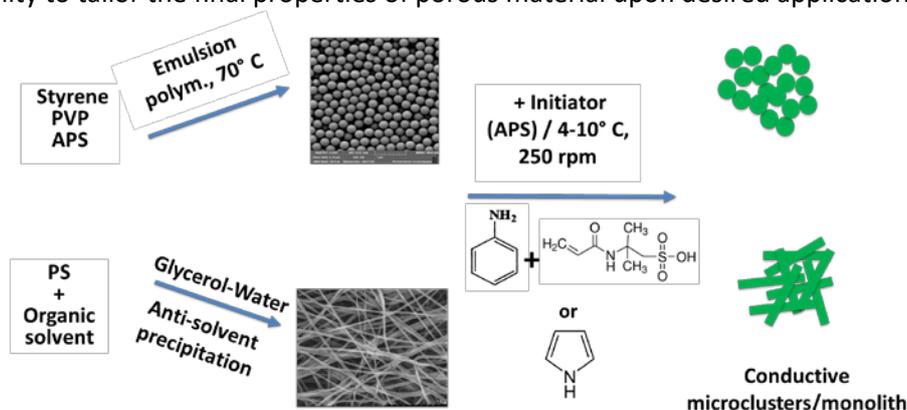
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In this work we investigate the effect of nanoparticle size and shape on the properties of porous materials. Initial step of the porous material preparation is the synthesis of polymeric nanoparticles of various sizes and shapes. An emulsion polymerization of styrene in the presence of polyvinylpyrrolidone was used to prepare spherical polystyrene nanoparticles (PS-NPs) with diameter ranking from 200 to 900 nm. In the case of polystyrene fiber-like nanoparticles, these were prepared by an anti-solvent precipitation of PS from the organic solvent in the highly viscose aqueous solution of glycerol. Once characterized, nanoparticles of both shapes were used as building blocks for synthesis of conductive porous material using a chemical oxidative polymerization of aniline-(2-acrylamido-2-methylpropanesulfonic acid) (ANI-AAAMPSA) and pyrrole in the presence of polystyrene nanoparticles (PS-NPs) (Figure 1). Systematic investigation of the NPs properties on the morphology and pore size distribution was carried out to improve our understanding of the controlling mechanisms including interactions of PS NPs with formed charged complexes or conductive monomers or oligomers. To do so, the ratio between ANI-AAAMPSA (or pyrrole) and PS-NPs, and ratio of ANI-AAAMPSA was varied considerably. Furthermore, both stagnant and flow conditions were used to prepare porous material in the form of microparticles or a monolith.

It was observed that both NP size and shape have strong impact on the porosity and pore size distribution of the prepared material, where larger particles resulted in larger pores. Furthermore, it was demonstrated that the surface morphology of the porous material is strongly dependent on the ratio PANI-PAAMPSA (or polypyrrole) / PS-NPs while the ratio of ANI-AAAMPSA strongly impacts the size of formed microclusters. In addition, it was found that for both conductive polymers the presence of PS NPs has positive effect on the morphology of conductive layer which cannot be obtained from conductive polymer alone. Over all it was found that porosities of up to 80% and surface areas between 10 to 20 m<sup>2</sup>/g, respectively, can be obtained by controlled assembly of PS-NPs in the presence of PANI-PAAMPSA (or polypyrrole). Thermal gravimetric analysis (TGA) confirmed a very high thermal stability of the prepared material up to 350 °C, while DSC results indicated that the conductive polymer coating serves as a thermal barrier for PS-NPs. Furthermore, the materials exhibited specific conductivities in the order of few mS/cm. Obtained results confirm possibility to tailor the final properties of porous material upon desired application.



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# Water-soluble naked gold nanoclusters are not luminescent

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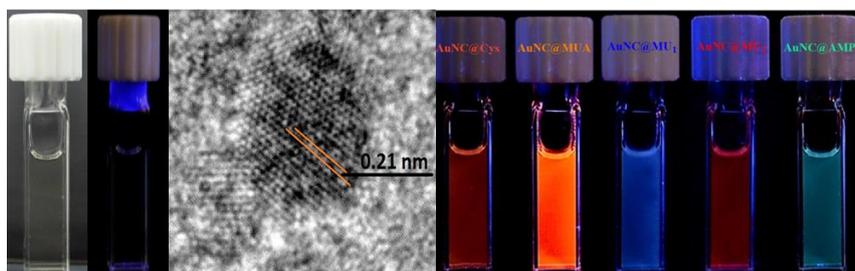
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Gold nanoclusters (AuNCs) are attractive systems due to their enhanced quantum confinement, which provides them with unusual optical, electronic, and magnetic properties [1]. They can exhibit strong photoluminescence and are biocompatible since they do not possess toxic heavy metals.

Many studies confirm that ligands play a key role in the AuNC structure and properties; the role of the ligands on the electronic and optical properties are the subject of debate [2]. The AuNC photoluminescence has been related to the presence of Au<sup>I</sup> at the nanocluster surface, and their strong photoluminescence is attributed to aggregation-induced emission of Au<sup>I</sup> complexes on the Au<sup>0</sup> core [3]. The most studied AuNCs are those passivated with thiols, where the Au<sup>0</sup> core is surrounded by a shell of Au<sup>I</sup>-thiolate complexes.

We present here the easily preparation of water-dispersible naked gold nanoclusters (AuNC<sub>naked</sub>), i.e. without organic capping, and show that they are non-luminescent (Figure 1) [4]. The AuNC<sub>naked</sub> were then easily passivated with different thiols and adenosine monophosphate to lead to luminescent NCs (Figure 1). This is an important finding as the photoluminescence of the passivated AuNCs can be now clearly attributed to the ligand-AuNC surface interaction.



**Figure 1** (left) Comparison between the image of a water dispersion containing AuNC<sub>naked</sub> under lab light and that under UV-light; (centre) HRTEM image of AuNC<sub>naked</sub> and distance between planes, characteristic of Au; (right) image of water dispersions of AuNC capped with cysteine (AuNC@Cys), 11-mercaptoundecanoic acid (AuNC@MUA), 11-mercaptoundecanol (AuNC@MU1, AuNC@MU2), and adenosine 5'-monophosphate (AuNC@AMP) under UV-light.

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# Plasmonic Monitoring of Surface Topography Effects on Biofilm Growth

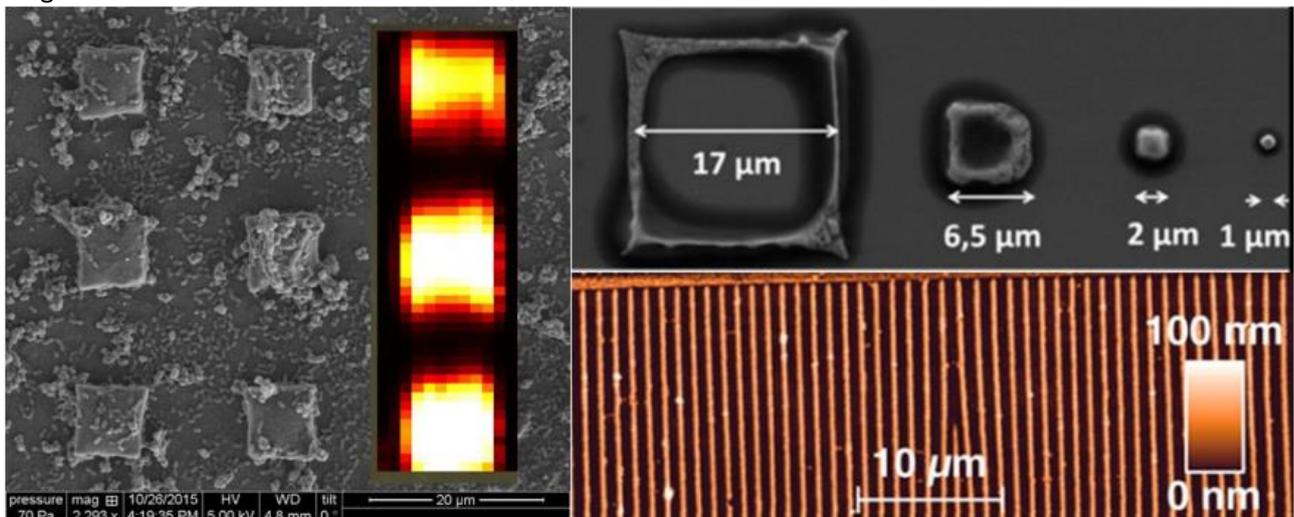
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The study of bacterial organization and biofilm formation has become an essential means for explanation of phenomena such as virulence, antibiotic resistance, long-term colony survival and propagation, and surface adhesion. Biofilm formation is facilitated by cell-cell communication processes known as quorum sensing, which enable collective behavior and metabolic coordination. Surface topography and chemistry play a significant role in bacterial adhesion and biofilm formation, and surfaces bearing micro- and nano-topographic features have shown improved resistance to biofouling. Current methods for monitoring quorum sensing in situ suffer limitations, thus we apply surface-enhanced Raman scattering to detect the vibrational spectra of quorum sensing molecules. Surface-enhanced Raman spectroscopy of bacteria grown atop plasmonic materials with structured topographic features gives insight into bacterial quorum sensing processes relevant to biofilm formation. The substrates are fabricated via templated colloidal self-assembly of gold nanoparticles followed by coating with a mesoporous silica layer for mitigation of signal contamination in complex media. The talk will give an overview of in situ Raman studies of bacterial quorum sensing, examples of anti-biofouling surface topographies found in the lab and nature, and discuss recent results towards improvement of anti-microbial surfaces and biomedical diagnostics.



**Figure 1** (left) *P. aeruginosa* grown on a micropatterned plasmonic substrate, SERS mapping of bacterial quorum-sensing inset, (right) Micro- and nano-structured plasmonic substrates. [1,2]

**Acknowledgements** The financial support of the European Research Council (Advanced Grant #267867) and the Spanish Ministry of Economy and Competitiveness (FJCI-2014-22598).

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# Two-Dimensional Magnesium Phosphate Nanosheets Form Highly Thixotropic Gels That Up-Regulate Bone Formation

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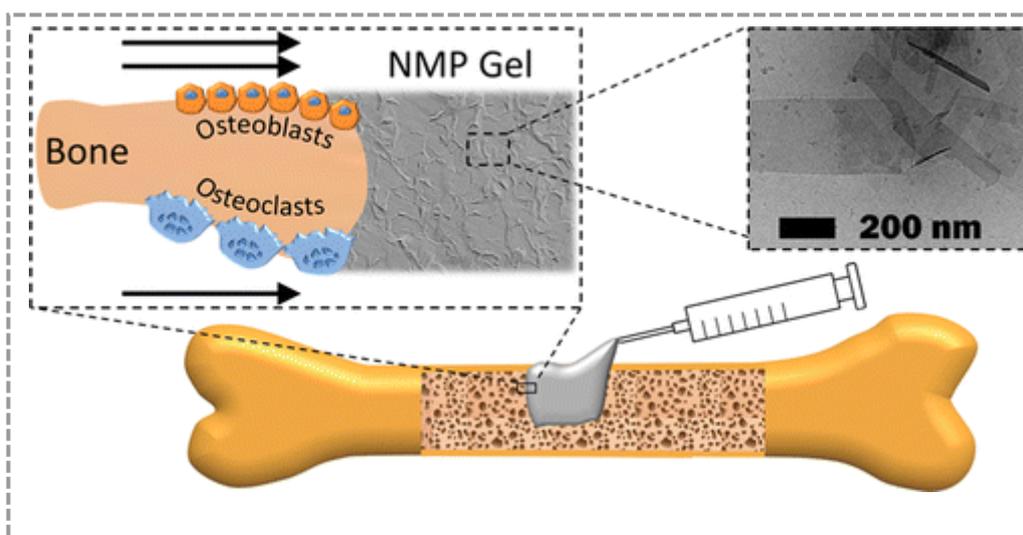
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Hydrogels composed of two-dimensional (2D) nanomaterials have become an important alternative to replace traditional inorganic scaffolds for tissue engineering. Here, we describe a novel nanocrystalline material with 2D morphology that was synthesized by tuning the crystallization of the sodium-magnesium-phosphate system. We discovered that the sodium ion can regulate the precipitation of magnesium phosphate by interacting with the crystal's surface causing a preferential crystal growth that results in 2D morphology. The 2D nanomaterial gave rise to a physical hydrogel that presented extreme thixotropy, injectability, biocompatibility, bioresorption, and long-term stability. The nanocrystalline material was characterized in vitro and in vivo and we discovered that it presented unique biological properties. Magnesium phosphate nanosheets accelerated bone healing and osseointegration by enhancing collagen formation, osteoblasts differentiation, and osteoclasts proliferation through up-regulation of COL1A1, RunX2, ALP, OCN, and OPN. In summary, the 2D magnesium phosphate nanosheets could bring a paradigm shift in the field of minimally invasive orthopedic and craniofacial interventions because it is the only material available that can be injected through high gauge needles into bone defects and fractures in order to accelerate bone healing and osseointegration. In addition, the high surface area of this material and its unique biocompatibility renders it ideal for many other biomedical applications such as decontamination of medical devices



**Figure 1** Graphical abstract depicting the structure of Magnesium Phosphate Nano sheets and its use for bone healing

# Perfluorocarbon-loaded Polymeric Nanoparticles with Unusual Structure for Multimodal In Vivo Imaging

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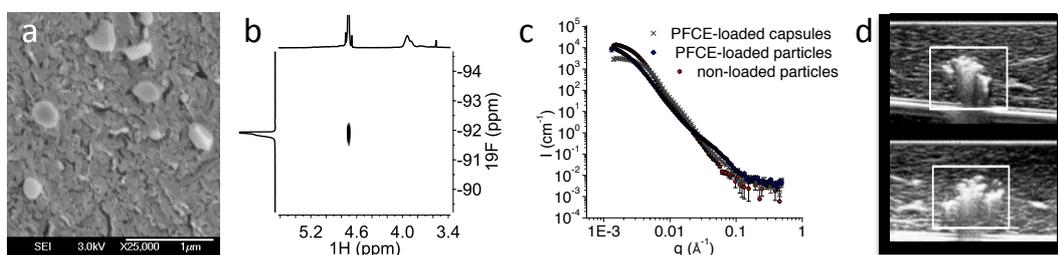
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Cellular therapies are promising for the treatment of currently non-curable conditions such as HIV or cancer. To improve these therapies monitoring of therapeutic cells is essential. Ultrasound (US) is a very attractive and patient-friendly imaging technique. Nevertheless, the low stability of imaging agents, with imaging periods in a time frame of milliseconds to minutes, limits the application of US for cell tracking.

We present perfluoro-15-crown-5-ether (PFCE) loaded polymeric nanoparticles (100 nm radius), which are suitable for long-term imaging with ultrasound in a range of days and for quantitative <sup>19</sup>F MRI.<sup>[1-3]</sup> Using a miniemulsion formulation process enables tailoring the colloidal properties to a desired application.

We extensively studied our nanoparticles with different physicochemical methods including multi-angle light scattering, cryogenic electron microscopy (Fig. 1a), solution 2D NMR (Heteronuclear Overhauser Enhancement Spectroscopy (HOESY, Fig. 1b)) and solid state NMR. Moreover, we measured Small Angle Neutron Scattering (SANS, Fig. 1c) at different solvent contrasts to highlight specific compartments of the particles using various controls. These results indicate that both the structure of our nanoparticles and the acoustic contrast generation mechanism are different from other colloidal US contrast agents. To assess the US performance of our particles, we measured US *in vitro* (Fig. 1d) and *in vivo*, and confirmed the results with <sup>19</sup>F MRI and fluorescence microscopy. Finally, we expect a clinical application of the nanoparticles in melanoma patients receiving dendritic cell therapy shortly.<sup>[4]</sup>



**Figure 1.** a) cryoSEM image of nanoparticles (scale bar 1000 nm). b) HOESY-NMR reveals that superhydrophobic PFCE is close to water. c) SANS patterns of PFCE-loaded particles compared to nanocapsules and non-loaded particles demonstrate structural differences. d) US images in tissue phantom 0 h (top) and 48 h (bottom) after injection.

**Acknowledgements:** ERC starting grant ERC-2014-StG-336454-CoNQUeST.

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# Controlled Assembly of Nanoparticle Mediated By Electrostatic Complexation With Long Polyelectrolyte Chains.

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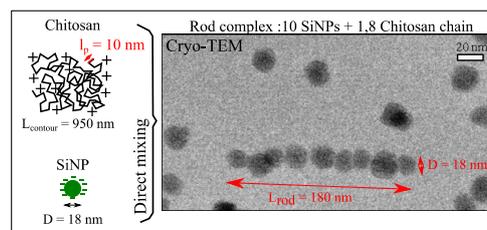
The structure of electrostatic complexes composed of oppositely charged nanoparticles and long polyelectrolyte chains (noted PEL) strongly depends on its degree of rigidity [1-4]. This is shown here on a large variety of nanoparticles (silica [1, 2, 3] or gold [4] with different radius  $R$ ) self-assemblies obtained by complexation with carefully selected oppositely charged PELs of different rigidity, which is quantified by the persistence length  $L_p$ .

We experimentally show that the ratio  $L_p/R$  is an important tuning parameter that controls the fractal dimension  $D_f$  of the nanoparticles self-assemblies, which is determined using small-angle neutron and small-angle x-ray scattering. For instance, in the case of silica nanoparticles:

(i) For  $L_p/R > 0.3$  (semiflexible chitosan and hyaluronan complexes), chain stiffness promotes the formation of one-dimensional nanorods (in excess of nanoparticles and at high ionic strength).

(ii) For  $L_p/R < 0.3$  (flexible poly-L-lysine), chain flexibility promotes easy wrapping around nanoparticles hence more ramified structures with  $D_f \sim 2$ , in good agreement with computer simulations.

(iii) Finally, ionic strength turned out to be another reliable mean of controlling  $D_f$  and the phase diagram behaviors. It finely tunes the interparticle potential, resulting in larger fractal dimensions at higher ionic strength [1-3]. Complete phase diagrams of the nanoparticle biopolyelectrolyte systems are presented and discussed.



**Figure 1** Naïve representation of individual components (left) before complexation and cryo-TEM picture (right) of a stable nanorod complex obtained after mixing in water. The indicated characteristics were derived from SAXS, SANS, light scattering and cryo-TEM investigations.

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# Design of Stable Nanocomposite Suspensions of Enzymatic Activity

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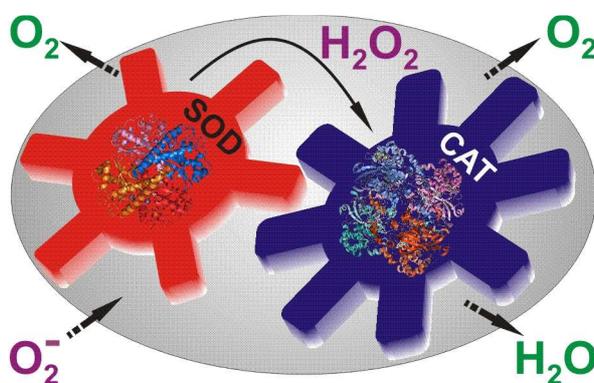
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Enzyme delivery in biomedical processes is challenging due to the complex environment in the biofluids. Immobilization of enzymes on nanoparticles may lead to successful targeted transport and can also protect the proteins against denaturation. However, colloidal stability has to be well-controlled since the aggregation of the carrier particles gives rise to inefficient delivery. Our research focuses on the immobilization of antioxidant enzymes (superoxide dismutase and catalase) on surface modified inorganic nanoparticles (layered double hydroxides [1], titania nanosheets [2] and titanate nanowires [3]) and on their formulation in aqueous suspensions.

For instance, we adsorbed superoxide dismutase on layered double hydroxide particles through electrostatic and hydrophobic interactions, as confirmed by IR spectroscopy and by determining the adsorbed amount with spectrophotometry. Colloidal stability studies performed by time-resolved dynamic light scattering and electrophoretic techniques revealed that the obtained materials possessed only limited stability against salt-induced aggregation. Coating the surface of the superoxide dismutase-layered double hydroxide composite with heparin (a natural anticoagulant polyelectrolyte of high line charge density) resulted in highly stable suspensions, even at high ionic strengths, where the traditional colloid theories predict rapid particle aggregation. We assume that the repulsive forces induced by the adsorbed heparin layer are of steric and electrostatic origin. The obtained hybrid nanocomposites showed sufficient enzymatic activity, i.e., neither protein immobilization nor polyelectrolyte coating processes decreased the superoxide radical anion scavenging activity.

Similar research is being performed with catalase enzyme and titania nanosheets or titanate nanowires. The final goal of this project is to develop enzyme cascades containing both superoxide dismutase and catalase confined in nanocomposites. In this way, complete decomposition of superoxide radical ions will be achieved (Figure 1) and the developed enzymatic systems will be promising antioxidant candidates for biomedical or other manufacturing processes, wherever the aim is to decompose reactive oxygen species in suspensions.

**Acknowledgements** Financial support by the Swiss Secretariat for Education, Research and Innovation, COST Action CM1303 and Swiss National Science Foundation is gratefully acknowledged.



**Figure 1** Cooperative function of superoxide dismutase (SOD) and catalase (CAT) enzymes.

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# Lipid-Alkylglycoside liposomes as a biocompatible vehicle: structural characterisation and future applications

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The consumer demands for functional food have increased the interest for encapsulation of bioactive compounds in the food industry. Encapsulation is crucial, since the bioactive compounds need to be protected from the environment and, in most cases, to be released at a given stage (and location) of the gastrointestinal tract. This requires that the delivery vehicle is biocompatible and also provides controlled release at a targeted location. The technology already available from the drug-delivery sector is taken as an inspiration but the high cost production needs to be reduced and new food-grade materials must be found. The liposome (lipid vesicle) concept is versatile, since the liposome features can be tuned to address the needs for encapsulation as well as targeting. The constituting building blocks, (natural) lipids forming bilayers, are non toxic and acceptable for foods.

The aim of the work is to develop liposome carriers containing an alkylglycoside surfactant ( $C_{16}G_8$ , 8 glucose unit head group and 16 carbons in the saturated alkyl chain). We thoroughly characterised the  $C_{16}G_8$  self-assembly with several techniques (e.g. DLS, SLS, NMR, SAXS, SANS) and we gained an exhaustive knowledge of its characteristics. It is well known that conventional alkylglycosides with smaller head-groups (glucoside, maltoside) affect bilayer permeability and vesicle integrity in a concentration-dependent manner. There are strong indications that these effects decrease with increasing length of the head-group. We optimised the lipid-surfactant vesicles preparation and we assessed the feasibility and stability of unilamellar vesicles (ULV) made of lipid and  $C_{16}G_8$  by DLS and SAXS experiments (Fig.1). We found that increasing molar ratio of surfactant leads to higher unilamellarity and stability of the vesicles. We fully characterised the vesicle structure with SANS as a function of the  $C_{16}G_8$  concentration and we gained information on the organisation of surfactant in the lipid bilayer. Complementary data on permeability were collected with NMR diffusion and dye leakage experiments.

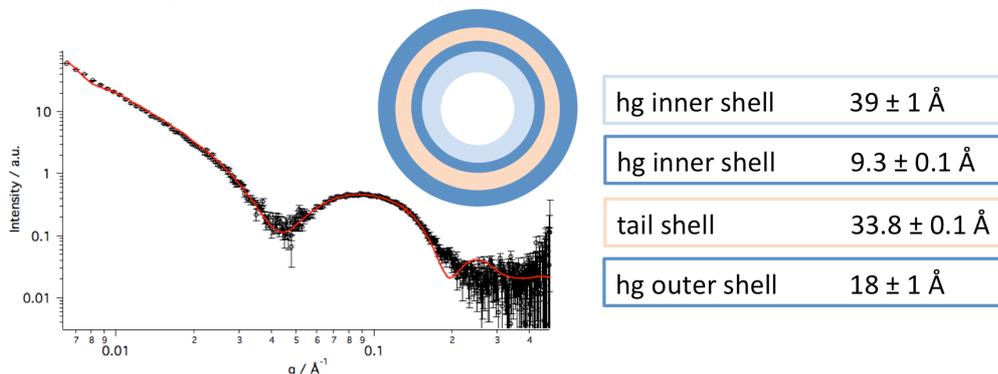


Figure 1 SAXS curves acquired with POPC-POPG- $C_{16}G_8$  (64:10:26 molar ratio) unilamellar vesicles (black circle). The model (red line) used to fit the experimental data was a 4 shells model with polydispersity. The fitted values of shell thicknesses are shown. The thicker inner shell shows very low contrast respect to the solvent. The shell thickness in the vesicle representation is exaggerated for clarity.

**Acknowledgements** This work has received funding from the People Programme (Marie Curie Actions) of the European Union's Seventh Framework Programme FP7/2007-2013/ under REA grant agreement n° 606713. The SANS study was allowed by allocations of beam time at ISIS and FRM II.

# Scattering Study on Small Unilamellar DMPC-Vesicles Incorporating the Saponin Escin

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1,2-Dimyristoyl-sn-glycero-3-phosphocholine (DMPC) belongs to the class of phospholipids and acts e.g. as a major membrane component. Therefore, model membranes consisting of DMPC mimic biological membranes quite well and allow to study effects of additives under different conditions, e.g. composition and temperature. Saponins are plant derived surfactants which occur among others in nuts and garlic and exhibit an amphiphilic structure built of a hydrophobic steroidal or triterpenic backbone with a varying number of hydrophilic sugar chains. Different saponins have a variety of pharmacological effects. However, on a nanoscale the interaction of saponins with biological membranes is not yet fully understood.

Therefore, in this study the effect of the pure saponin escin from horse chestnut tree on small unilamellar vesicles of DMPC, prepared by extrusion, is investigated mainly by different scattering methods in dependence on the escin amount and the temperature. An incorporation of escin above a critical amount can be deduced from the investigated parameters, namely the thermal phase transition temperature and vesicle size parameters like the radius, membrane thickness and lipid head-to-head distance within one monolayer. In addition to wide and small angle scattering we use neutron spin-echo spectroscopy (NSE) to analyze membrane mechanics at different escin contents.

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# Macro- and microscopic phase behaviour in metal-extracting water-poor microemulsions

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Solvent extraction as a separation procedure is a promising method for retrieving rare earths from electronic waste. However, an optimized process on an industrial scale has not been established. One major reason is the lack of fundamental knowledge, therefore designing a cost-efficient, adaptive and predictive formulation is still out of scope of possibilities. In order to gain a more comprehensive view on ternary phase diagrams (macroscopic view) and on the self-assembling properties of extractants in such media (colloidal view at nanoscale), we used a supramolecular approach to interpret complex formation in such phases [1].

For this study, we specifically designed a reference model using *Bis-(2-Ethylhexyl) phosphoric acid (HDEHP)* and its sodium salt *NaDEHP* (adopting the function of an extracted ion). To evaluate the solubilization properties of this model, we employed a Gibbs phase prism, where the z-axis shows the counter-ion variation of the extractant, thus representing the “efficacy” of an extraction (see figure 1). We show that counter-ion variation and the polarity of the apolar diluent have a huge impact on phase properties.

In order to correlate the macroscopic behaviour with the self-assembling properties of the extractant, we explored Winsor 2 and Winsor 4 phases with small angle scattering of neutrons and X-rays. This allows deducing size, shape and possible interactions between aggregates, as well as structuring into higher-ordered meso-structures. Neutron scattering was of particular interest to probe the penetration properties of different solvents, which affects the geometry of a cluster and their possibility to interact with each other.

With this novel approach of coupling the solubilization properties with aggregate formation, this work aims to elucidate the relation between mesoscopic structuring and macroscopic phase properties. As such, it contributes to a more complete understanding of phase behaviour in liquid-liquid extraction and permits chemical engineers to optimize the extraction phases.

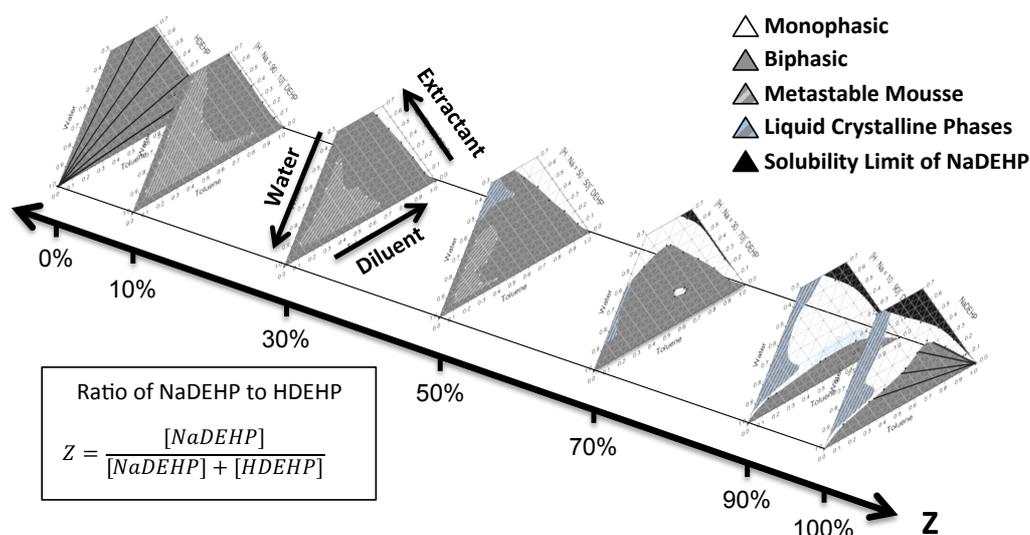


Figure 1 Gibbs phase prism of HDEHP, NaDEHP, water and toluene in weight-fractions.

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# Analytical and numerical models in kinetics of aggregation and relaxation in surfactant solutions: recent results

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A review of analytical and numerical results on the kinetics of aggregation and relaxation in micellar solutions of nonionic surfactants obtained by the authors [1-9] over the past 5 years is presented. The results had been found on the basis of the analytical and direct numerical solution of the continual and discrete Becker-Döring kinetic equations for the molecular mechanism of aggregation via additions and emissions of a single molecule of surfactant [1-5,8,9] and on the basis of the discrete generalized Smoluchowski equations for the mechanism of fusions and fissions of micelles [6,7]. Various possible aggregation and relaxation mechanisms at all times scales have been considered in detail: from the times of ultrafast relaxation of small oligomers to the times of fast and slow relaxation of micelles. Based on the droplet and quasi-droplet, linear, and interpolation models for the work of aggregation, a linear and nonlinear dynamics of the restructuring of micellar systems, consisting of spherical, cylindrical and coexisting spherical and cylindrical aggregates, had been studied.

A special attention has been paid to the quality of the continual Fokker-Planck form of the Becker-Döring kinetic equations for the molecular mechanism of aggregation and its application to description of the stages of fast [8] and slow [9] relaxation. The specific times of these stages can be found from the experiment [10], and we need to improve the accuracy of their theoretical prediction. An analytical expression for the characteristic time of slow relaxation turned out to be in good agreement with the results of numerical solution of the difference Becker-Döring equations [1] in a wide range of total surfactant concentrations. However, the analogous agreement for the characteristic time of fast relaxation requires an extension of the Fokker-Planck form of the Becker-Döring kinetic equations. The numerical solution of the difference Becker-Döring equations allows us to find the appropriate time-dependent contribution to the equilibrium distribution of molecular surfactant aggregates on the aggregation number, which effectively attenuates after slow relaxation. Finding the form of this term in the analytical theory, i.e., finding the time-dependent distribution of aggregates in the axis of aggregation numbers between maximum and minimum of the aggregation work, requires taking into account variation of concentration of surfactant monomers due to significant exchange by monomers between the molecular aggregates. Previously, this task had not been realized. In this communication, we derived an analytical expression for the previously unknown fine structure of the mode of slow micellar relaxation in the aggregation number region between the maximum and the minimum of the aggregation work. The resulting expression was used to reveal the similar fine structure of the aggregation rates at different points in the same aggregation number region, where aggregation rates are small, but demonstrate an interesting non-monotonic behavior. Found analytical relations for the slow mode and aggregation rates were tested using numerical solution of the difference Becker-Döring equations.

**Acknowledgements** This work was supported by the Russian Science Foundation (Grant No. 14-13-00112).

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# Water-in-oil microemulsions with encapsulated nisin: Effect of additives on structure and efficacy

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During the last decades, much attention has been paid on the replacement of high energy methodologies for the use of bacteriocins, peptides with antimicrobial characteristics, and the enhancement of their effectiveness as food preservatives.<sup>1</sup> In the present study, water-in-oil (W/O) microemulsions based on refined olive oil (ROO) or sunflower oil (SO) and distilled monoglycerides (DMG) were effectively formulated. Small Angle X-ray Scattering (SAXS), Electron Paramagnetic Resonance (EPR) spectroscopy and Dynamic Light Scattering (DLS) were used to structurally characterize the proposed nano-carriers. A spherical core-shell model with a hard sphere structure factor model was selected to best fit to the  $I(q)$  from the obtained SAXS patterns. On the other hand, simulation of the EPR experimental spectra indicated the transition of the spin probe from fast to slow motion *via* structural modulations.<sup>2</sup>

To further optimize the above systems, ethanol or propylene glycol have been added to the systems in specific amounts. Essential oils of Greek origin have been, finally, used to enhance the antimicrobial properties of the systems. It was found that the addition of essential oils increased the monophasic region of the microemulsions both in the presence and absence of nisin. Ethanol addition resulted to U-type microemulsions whereas propylene glycol resulted to a more rigid surfactant monolayer.

The antimicrobial effect of the encapsulated nisin was evaluated using the Well Diffusion Assay (WDA) technique against pathogens such as *Staphylococcus aureus*, *Listeria monocytogenes*, *Bacillus cereus* and *Escherichia coli*. Significant alterations on the efficacy of the systems were observed with the addition of oregano, thyme, dittany or rosemary essential oils. Also, the nisin loaded systems were found efficient when tested in infected lettuce and minced meat.

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# Phase and Shape Transitions of Surface-Polymer-Controlled Phospholipid Systems

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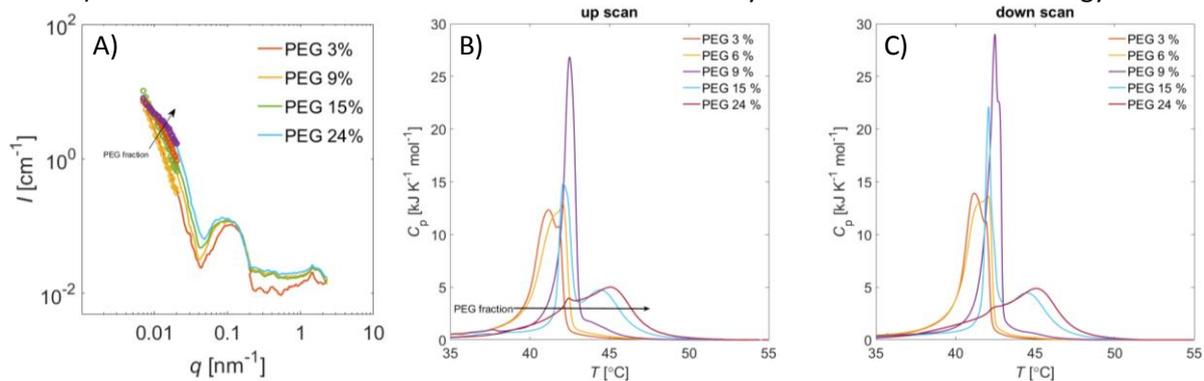
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Liposomes can be used as drug carriers that can be engineered to function in site-specific drug delivery when they are functionalized with targeting ligands (e.g., peptides, aptamers and antibodies). Polyethylene glycol (PEG) is used to increase the biocompatibility; to prolong the circulation times of liposomes in blood, and to maintain the integrity of the drug delivery systems in storage. The prolonged life span is obtained by the increased repulsive interaction between the PEGylated lipids. As the PEG-moieties show repulsion against other similar units, the liposome surface is exposed to steric pressure and fluidity changes may occur when the PEG fraction is increased. In addition, the curvature in the lipid bilayer is changed due to the large head group in the PEGylated lipids, causing a mismatch in the lipid domain, and a change in the overall shape towards a new minimum energy form of e.g. spherical micelles, liposomes, tubular structures, or bicelles that can be used in various applications. [1,2] Since the lipid bilayer is also a temperature sensitive system, and the thermal phase transition of melting and freezing can have different kinds of kinetics, the phase diagram of such systems can prove rather complex.

In this work, we have studied the phase behavior of the DPPC:DSPE-PEG(X) system with cryo-TEM, dynamic light scattering, differential scanning calorimetry, diffusion NMR, SAXS (Fig 1A) and WAXS as a function of temperature and PEG fraction to determine the morphology of the lipid vesicles and the fluidity in the lipid bilayer. The results are used to build up a phase diagram and to determine how two distinct sets of DPPC lipids are present at the rim region, next to the curved DSPE-PEG lipids, and at the central area. The raft-like appearance is apparent as the phase transition temperature is increased for the rim lipids (Fig.1B and 1C). This effect is discussed in terms of statistical thermodynamics and curvature energy.



**Figure 1** A) Small angle scattering of different PEG fraction. Change in the slope at low  $q$  shows a change in the shape of the vesicle. The DSC up (B) and down (C) scans of lipid systems containing 3, 6, 9, 15 and 24 mol % of PEGylated lipid show a shift in the phase transition temperature. The appearance of the second peak at higher temperature indicates a shift in the shape and separation of two sets of DPPC behaviours at the rim and at the centre of the discoid areas.

**Acknowledgements** The financial support of TEKES is acknowledged for funding via the “Light Activated Drug Delivery Systems” program.

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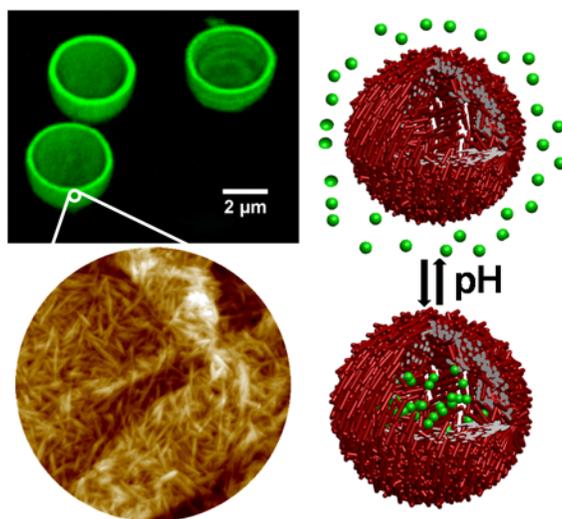
# Cellulose Nanocrystal Microcapsules as Tunable Cages for Nano- and Microparticles

Chunhong Ye<sup>1,2</sup>, Sidney T. Malak<sup>2</sup>, Kesong Hu<sup>2</sup>, Andreas Fery<sup>1</sup>, Vladimir V. Tsukruk<sup>2</sup>

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We demonstrate the fabrication of novel microcages with large and through pores using sole biocompatible and biodegradable all natural cellulose nanocrystals (CNC) via Layer-by-Layer self-assembly, which indicates a highly open “haystack” shell morphology (Figure 1). In strike contrast to conventional polymer LbL microcapsules with limited molecular-level permeability, the resilient cage-like microcapsules show a remarkable open network morphology that facilitates across-shell transport of large solid particles with a diameter from 30 nm to 100 nm. Moreover, the transport properties of solid nanoparticles through these shells can be pH-triggered without disassembly of these shells. Such behavior allows for the controlled loading and unloading of solid nanoparticles with much larger dimensions than molecular objects reported for the conventional polymeric microcapsules<sup>[1]</sup> And the CNC capsules indicate remarkable stability in extreme acidic and basic conditions. These cellulose nanocrystal microcapsules with controlled across-shell transport and high open porosity present a novel candidate for prospective functional materials relevant to prospective applications in bioengineering for controlled encapsulation of solid nanoparticles with nanoscale and sub-micron dimensions.



**Figure 1** Hollow microcapsules with “haystack” morphology composed with densely packed individual cellulose nanocrystals.

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# Spreading of liquids over porous substrates

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We present a current state of research in the area of simultaneous spreading and imbibition of droplets over porous substrates. It is shown that spreading/imbibition is substantially different in the case of complete [1,2] and partial wetting [3,4]: stages of spreading/imbibition are very much different in these two cases (Fig. 1). The latter difference is caused by the presence of contact angle hysteresis [3].

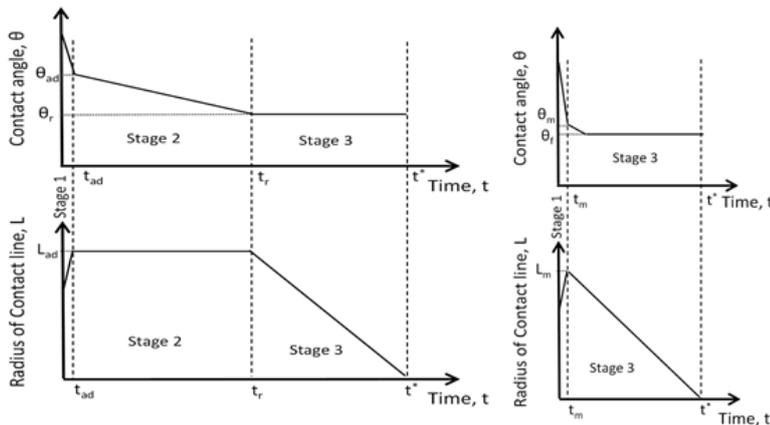


Fig. 1. Spreading/imbibition of a droplet over porous substrates a) partial wetting case: three stages.  $L_{ad}$  is the maximum radius of droplet base,  $\theta_{ad}$  is the advancing contact angle,  $t_{ad}$  is the time when  $\theta_{ad}$  is reached;  $\theta_r$  is the receding contact angle,  $t_r$  is the time when  $\theta_r$  is reached and  $t^*$  is the time of droplet disappearance; b) Complete wetting case: there are two stages.  $L_m$  is the maximum value of droplet base radius,  $t_m$  is the time when  $L_m$  is reached,  $\theta_m$  is the contact angle at  $t_m$ ,  $t^*$  is the time of droplet disappearance and  $\theta_f$  is the final contact angle at  $t^*$ . Note, the stage 2 is absent in complete wetting case.

Originally the theory of simultaneous spreading/imbibition over porous substrates was developed for the case of droplets of Newtonian liquid [1]. A remarkable universal behaviour of time dependences of wetting diameter, droplet base and contact angles was predicted and experimentally verified. However, a number of liquids (the most important blood, as well as, polymeric solutions used in cosmetic industry) show power law shear thickening non-Newtonian behaviour. The theory was generalized for the case of this kind of non-Newtonian liquids. The spreading/imbibition of blood droplets [1-4] over filter paper and polymeric solutions [5] over hair tresses showed a good agreement with the theory predictions.

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# An ATR-FTIR based method for dynamic analysis of wetting transitions on superhydrophobic nanostructured surfaces

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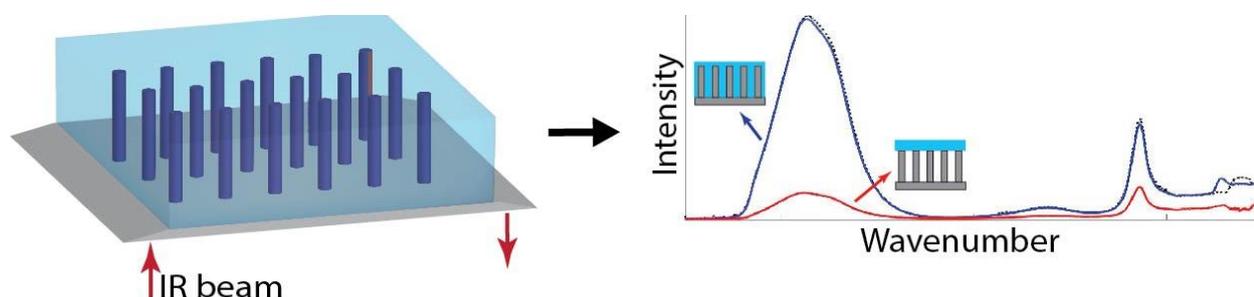
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Wetting behavior on a surface is a typical interfacial phenomenon dictated by the surface morphology and the liquid-solid-air interactions at the nanoscale [1]. Understanding the wetting behavior of nanostructured surfaces is crucial for the development of electronic and nanofluidic devices as well as for the design of self-cleaning surfaces. In the present work we explore the stability of Wenzel and Cassie-Baxter states and the dynamics of superhydrophobic breakdown on functionalized nanopillar arrays.

With a novel application of ATR-FTIR, in-situ wetting of the surface can be accurately characterized. ATR-crystals are prepared from patterned wafers by mechanical polishing and are immersed in liquid. The pillars are ~260 nm high and ~40 nm in diameter and are rendered superhydrophobic by functionalization with FDTS. Air layers present in between the structures, as for the Cassie-Baxter state, attenuate the evanescent waves that emerge from the crystal. IR-bands at high wavenumbers are relatively more sensitive to this attenuation than those at low(er) wavenumbers owing to their shorter penetration depths. Consequently, spectra of Wenzel and Cassie-Baxter wetting states show different peak intensity ratios for the water bending ( $1640\text{ cm}^{-1}$ ) and stretching ( $3380\text{ cm}^{-1}$ ) bands and can thus accurately be distinguished. This technique is used to study the stability and breakdown of superhydrophobic states. The liquid surface tension was reduced by addition of isopropanol to the aqueous solution. ATR-FTIR resolved different zones of the Cassie-Baxter and Wenzel states as a function of the liquid surface tension, as well as a transition region with time-dependent partial wetting. This method is the first demonstration of using ATR-FTIR for in-situ wetting studies on nanostructured substrates and can be extended towards realtime analysis of wetting kinetics, hysteresis and reversibility.



**Figure 1.** Schematic representation of the ATR-FTIR set-up and spectrum interpretation.

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# Decreasing the wettability of cellulose nanocrystal surfaces using wrinkle-based alignment

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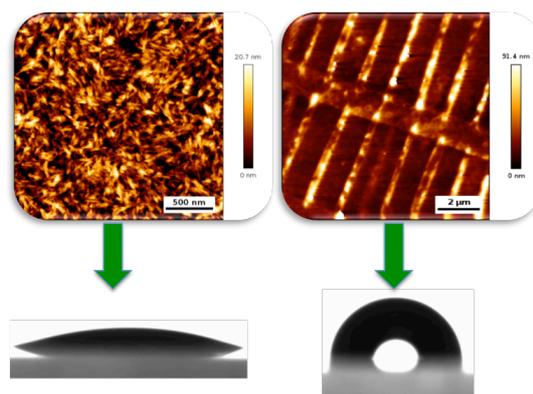
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Cellulose nanocrystals (CNCs) are a particularly appealing format of the natural biopolymer due to their exceptional strength, nanoscale dimensions and needle-like shape anisotropy [1]. However, CNCs are hydrophilic and hence their wettability makes them impractical for many coating applications [2], with various approaches using chemical functionalisation to overcome this. Here we show that CNC-coated surfaces can be rendered apparently hydrophobic by alignment of the native CNCs using a wrinkled template-mediated printing process [3]. We present a novel and simple method allowing full release of the CNCs from the template and their permanent adsorption into fine patterns onto the surface, thus preventing CNC repositioning during wetting. The aligned CNCs induce strong pinning effects that capture and retain water droplets with high contact angle and large roll-off angles, without becoming susceptible to oil contamination. The fabrication process for these coatings could be achieved by large-scale printing, making them a practical and cost-effective solution to hydrophobic coatings from raw cellulosic materials.



**Figure 1** The wettability of a water droplet changes from hydrophilic (bottom left) to hydrophobic (bottom right) when the cellulose nanocrystals are aligned (top right) compared to a random state (top left).

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# Hysteresis of Contact Angle of Sessile Droplets on Deformable Substrates: Influence of Disjoining Pressure

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Liquid droplets deposited on a deformable/soft substrate can cause the substrate to deform. Surface forces near the three-phase contact line and substrate's elasticity determines both the shape of the substrate after deformation and the liquid profile. A theory of contact angle hysteresis of liquid droplets on deformable/soft substrate is developed in terms of disjoining pressure isotherm,  $\Pi(h)$ , which accounts for the action of surface forces in the vicinity of the three-phase contact line. Disjoining pressure isotherm is s-shaped, which determines all features of both droplet and deformable substrate. Elasticity of the substrate is described with the help of simple Winkler's model for elastic surfaces [1]. The obtained results are in good agreement with the contact angle hysteresis theory developed earlier for non-deformable substrates in terms of disjoining pressure isotherm and quasi-equilibrium phenomena [2]. It is shown that the properties of disjoining pressure isotherm greatly affect the substrate deformation and hysteresis properties. Both advancing and receding contact angles are dependent upon volume of the droplet (which has a direct experimental confirmation) and are unique to the physical characteristics of the liquid-substrate system. As expected advancing and receding contact angles of droplets on deformable substrates are calculated to be less than on a non-deformable substrate. Receding contact angle is estimated to be closer to the equilibrium contact angle as was predicted for non-deformable substrates. This conclusion is in contradiction to the commonly used assumption of advancing contact angles as first approximation of equilibrium contact angle. Advancing and receding contact angles reduce with increase in volume of the droplet.

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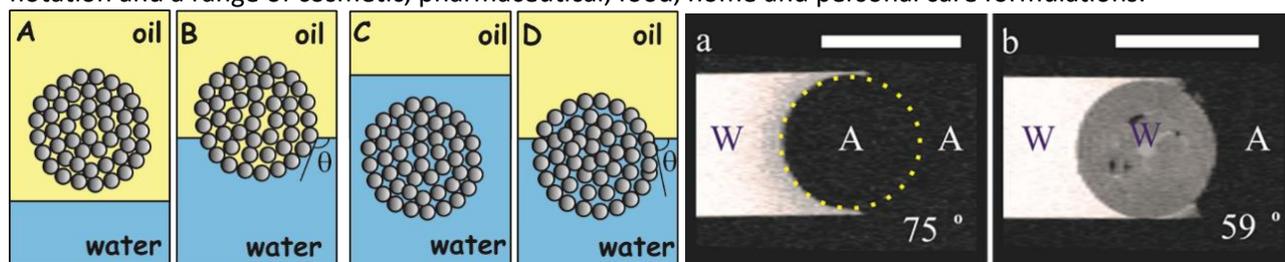
# Preparation and attachment of composite porous supra-particles to liquid interfaces: Theory and experiment

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We have developed and experimentally tested a theoretical model of the attachment of fluid-infused porous supra-particles to a fluid-liquid interface [1]. The model considers the wetting behavior of agglomerated clusters of particles, typical for powdered materials dispersed in liquid, as well as for the adsorption of liquid-infused colloidosomes at the liquid-fluid interface. The free energy of attachment of a composite spherical porous supra-particle made from much smaller aggregated spherical particles to the oil-water interface was calculated. Two typical cases were considered: (i) a water-filled porous supra-particle adsorbed at the oil-water interface from the water phase, and, (ii) an oil-filled porous supra-particle adsorbed at the oil-water interface from the oil-phase. We derived the connection between the three-phase contact angle of the small “building block” particles and the contact angle of the liquid-infused porous supra-particles. The theory predicts that the porous supra-particle contact angle attached at the liquid interface strongly depends on the type of fluid infused in the particle pores and the fluid phase from which it approaches the liquid interface. We tested the theory by using millimetre-sized porous supra-particles fabricated by evaporation of droplets of polystyrene latex microparticle suspension on a pre-heated super-hydrophobic surface, followed by thermal annealing at the glass transition temperature [2]. Such model porous particles were initially infused with water or oil and approached to the oil-water interface from the infusing phase. The results from our experiments show that when adsorbing at the hexadecane-water interface, the porous supra-particles behaved as hydrophilic when they were pre-filled with water and hydrophobic when they were pre-filled with hexadecane. The results which are in line with the theoretically predicted contact angles for the porous composite supra-particles based on the values of the contact angles of their building block latex particles measured with the Gel Trapping Technique [1]. The experimental data for the attachment of porous supra-particles to the air-water interface from both air and water also agree with the theoretical model. This study gives important insights about how porous particles and particle aggregates attach to the oil-water interface in Pickering emulsions and the air-water surface in particle-stabilized aqueous foams that are relevant in ore flotation and a range of cosmetic, pharmaceutical, food, home and personal care formulations.



**Figure 1.** LHS: Scheme of a supra-particle attached to the oil-water interface and infusion of the porous particles by one of the liquid phases on their attachment. (A) A porous supra-particle filled with oil and (B) attached to the oil-water interface. (C) A supra-particle filled with water and (D) attached to the oil-water interface. The same applies for the air-water interface for pre-wet and for dry porous particles. Note that the same porous particles may have different effective contact angles depending on the infused fluid before their attachment to the liquid interface. RHS: MRI images of composite porous supra-particles made from 2.5  $\mu$ m sulphate latex particles suspension by the evaporation and thermal annealing method. The image shows the position of the air-water (A-W) surface on the porous particle surface. (a) A dry supra-particle attached at the A-W interface; pores are filled with air, as the air shows a dark region; (b) a water infused supra-particle attached to the A-W interface; water inside the porous particle is seen in grey color.

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# Can long-chain alcohols be used as antifreeze for aqueous droplets on hydrophobic surfaces?

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Recent advances in the control of surface wetting lead to the development of the diversity of functional materials with the special wettability for industrial applications. Hydrophobic and superhydrophobic surfaces have aroused researchers' intense interests due to their importance in both academic science and practical applications. One of the key points for academic studies is the behavior of such surfaces in outdoor conditions of exploitation where the organic airborne contaminations are ubiquitously present. Typically such contaminations act as surfactants for aqueous medium/air and aqueous medium/solid interfaces. We have studied the effect of contact of hydrophobic and superhydrophobic surfaces with the vapors of long-chain saturated alcohols on the anti-icing ability of considered surfaces. Our theoretical and experimental analysis has shown that long-chain alcohols may serve as antifreeze for aqueous droplets on hydrophobic surfaces. We will discuss physics underlying this phenomenon and will show that three different physico-chemical mechanisms have to be accounted for such action of alcohols. The first mechanism is related to suppression of water evaporation due to the formation of a monolayer on the droplet surface, resulting in a decrease in the droplet supercooling at negative temperatures. The second mechanism is associated with the shift of triple point for the water boundary layers at aqueous medium/air and aqueous medium/solid interfaces. And the last one is responsible to the hindering of heterogeneous ice nucleation due to a decrease in the area of contact between aqueous droplets and the hydrophobic/superhydrophobic substrate. The experimental data convincingly proving the theoretical analysis and the importance of abovementioned mechanisms will be presented.

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# Interaction of water with the Gypsum (010) surface: a study by SFG vibrational spectroscopy and *ab initio* MD simulations

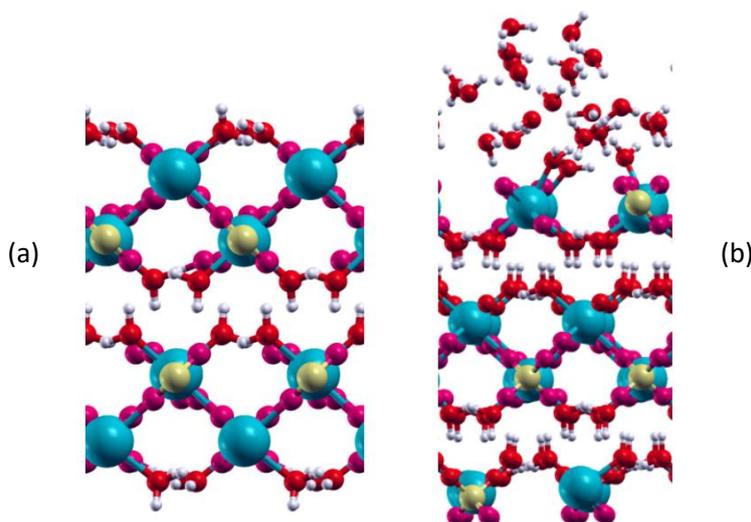
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Gypsum is an abundant, low cost mineral, which is widely used in the construction industry (“plaster of Paris”) and is also biocompatible [1]. Recently a new preparation method that yields gypsum parts with enhanced mechanical properties has been demonstrated [2], and the high strength was attributed to the presence of ultrathin confined water layers among compacted gypsum microcrystals. Here we present a combined experimental/theoretical study which provides a molecular-level understanding of the gypsum/water interface. We investigated the structure and dynamics of adsorbed water from vapor at room temperature on a (010) gypsum single crystal surface, by combining Sum Frequency Generation (SFG) vibrational spectroscopy [3] and *ab initio* molecular dynamics (MD) simulations. The SFG spectra of gypsum in low relative humidity (RH  $\sim$  0.1%) showed anisotropic arrangement of (structural) surface H<sub>2</sub>O molecules and the presence of dangling OH groups, as shown in the simulated structure of Figure 1(a). At higher RH the adsorbed water also revealed an anisotropic arrangement, but with the free OH signal significantly suppressed. The excellent agreement between the calculated and measured vibrational spectra validates the theoretical methodology. Thus, the MD simulations could provide further insights into the surface structure that could not be obtained only from the experiments, such as the structures of thicker water films (Figure 1(b)).



**Figure 1** Simulated structures for the gypsum (010) surface interacting with different water surface coverages: (a) 1ML - one monolayer - of (structural) water; (b) 3ML of adsorbed water.

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# Centipede and comb polymers at air-water interface

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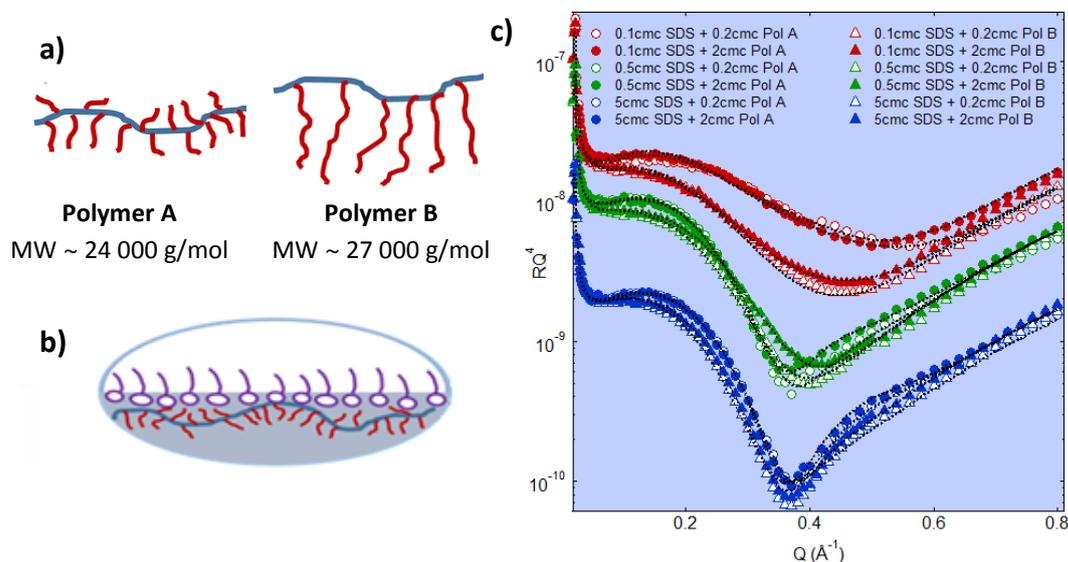
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Understanding interfacial structures of polymer/surfactant mixtures is of fundamental and practical importance. A key parameter governing the polymer-surfactant interactions is the polymer architecture. Here, we have studied two neutral co-polymers with a *centipede* and *comb* structure respectively, both with a *hydrophilic* PEG backbone but differing lengths and densities of *hydrophobic* PVAc grafts (Fig 1). Synchrotron X-ray reflectivity and neutron reflectivity results show that a ~2 nm thick layer is formed at the air-water interface by the polymers, with intricate interactions with surfactants (C<sub>12</sub>TAB, C<sub>12</sub>E<sub>5</sub>, SDS), when present. The results suggest competitive adsorption at the air-water interface, where the polymers are depleted from the interface by surfactants, with the surfactant charge playing an important role in the process. These results are further complemented by surface tension measurements and foam analysis, in order to establish a link between the structural parameters (*e.g.* polymer molecular architecture, surfactant charge, molecular weight, and hydrophobicity) and the complex polymer/surfactant interfacial behaviour governing their performance in a plethora of industrial applications. A brief comparison to a family of dendritic co-polymers comprising of a PEI core and PEG branches has also been initiated, providing further insight into the importance of the polymeric architecture in these systems.



**Figure 1** a) Schematic representation of a centipede Polymer A and a comb Polymer B. b) Schematic representation of the fitting model comprising of 3 layers at the air-water interface: surfactant chains, surfactant heads, and a polymer. c) Fitted XRR data of mixed polymer/surfactant systems highlighting the difference between mixtures of Polymer A and Polymer B with SDS, especially at low surfactant concentrations. At high surfactant concentrations, both polymers are depleted by the surfactant. The data for different concentrations is offset for clarity.

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# Mixtures of solid nanoparticles at water-air interfaces

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Solid nanoparticles (NPs) dispersed in aqueous media have been widely employed in many application fields and, among them, as stabilizers of foams and emulsions. Depending on their composition, surface charge, morphology, size and, in many cases, in association with specific surfactants, NPs assume adequate amphiphilic properties, which favour their transfer to the liquid interfaces [1, 2]. Particle stabilized foams, present unique properties related to the control of stability and morphology. These peculiarities make them appealing also in the field of materials processing, for example, for the fabrication of porous materials with tailored structural properties [3].

In this work, we investigate the surface properties of aqueous dispersions containing solid nanoparticles of different nature, associated to short chain ionic surfactants. In particular, we investigated Titanium dioxide (TiO<sub>2</sub>) and colloidal silica particle (SiO<sub>2</sub>). TiO<sub>2</sub> is widely used in many technological fields, due to its important optical feature like, for example, photocatalytic properties and UV resistance, while SiO<sub>2</sub> has been widely investigated and its behaviour at liquid interfaces is rather well established [4].

The selective adsorption of these two systems at the water-air interfaces has been systematically investigated by surface tension and dilational rheology measurements. The results obtained, crossed with those by bulk characterization via Dynamic Light Scattering (DLS) and  $\zeta$ -potential measurements, allow us to understand the role of the dispersion formulation and, in particular, of the cationic surfactant in the determination of the structure of the mixed layers at the water- air interfaces.

On the bases of this surface and bulk characterisation, particle-stabilized foams with different lamella structure have been obtained with these systems and analysed against the dispersion composition.

The use of mixtures of nanoparticles of different chemical compositions to generate and stabilize foams is a rather innovative topic. In particular, the TiO<sub>2</sub> - SiO<sub>2</sub> association looks very promising for the application to the production of solid foams with specific functional properties.

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# Nanoparticle-induced membrane domain formation in double emulsion templated lipid vesicles

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The interaction between functional nanoparticles and lipid membranes has received increasing attention because of the multiple potential applications of nanoparticles in biomedicine and pharmacy. For example, the controlled incorporation of hydrophobic nanoparticles in the membrane of vesicles intended for use as drug delivery vehicles may enable finely tuning the permeability, structure and mechanical properties of these membranes and thus ultimately controlling drug release [1]. Moreover, if nanoparticles are either plasmonic or magnetic, drug release may be triggered by external stimuli such as light or magnetic fields [2]. Unfortunately, it is difficult to load lipid membranes with a controlled number of hydrophobic nanoparticles using conventional methods for vesicle production. Instead, we propose the use of water-in-oil-in-water double emulsion drops, fabricated using glass-capillary microfluidic devices, as templates to form vesicles that incorporate a controlled number of hydrophobic nanoparticles in their membranes [3]. In particular, we fabricate vesicles with membranes composed by a mixture of a single type of lipid, which is in the fluid state at room temperature, 1-palmitoyl-2-oleyl-sn-glycero-3-phosphocholine (POPC), and hydrophobic gold nanoparticles with a typical diameter of about 4 nm. In this microfluidic approach, removal of the oil that initially forms the shells of the double emulsions results in the formation of a hybrid lipid/nanoparticle membrane. The resultant vesicles are monodisperse in size, owing to the size of the double emulsion templates, and have uniform internal and membrane compositions. Importantly, we observe the formation of solid domains in these membranes, despite they are composed by a single-type lipid in the fluid state. The versatility of the microfluidic approach presented here to the fabrication of vesicles with hybrid lipid/nanoparticle membranes together with the observation of domain formation in these vesicles may open the venue to very subtle engineering of lipid vesicles.

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# Biomolecules absorbing at air-liquid and liquid-liquid interface.

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Adhesion and absorption of biomolecules to liquid hydrophobic interfaces is a key issue in bio-surfaces science and applications.

An extremely sensitive interferometer based on oscillating bubbles and drops allows to study the mechanical properties of liquid interfaces. The resonance frequencies of the bubble or drop are excited by means of a frequency-sweeping alternating electric field of low intensity, and the response of the system is obtained in the regime of linearity. The central frequency of the resonant modes and their width allow to access the surface (interface) tension and the local viscosity on the few-angstrom lengthscale. Besides, the amplitude of the induced oscillations is a putative measure of the net interfacial charge [1].

The change in a drop or bubble resonance parameters is now studied during absorption of very low amounts of additives to their surface [2].

We report the evolution of the interfacial tension of an immiscible squalene drop in water, showing that the progressive addition of very small amount of a biosurfactant (hundred times lower than the cmc in bulk) induces at some point a sharp process that can be interpreted as a gas-to-liquid transition of the monolayer at the interface. Moreover, we show that it is possible to follow the kinetic of absorption of proteins on the surface of an air bubble in water, when the bulk concentration is extremely low. Well before the lowering the surface tension, we trace the modification of the net charge at the interface simply by measuring the change of the resonant oscillation amplitude.

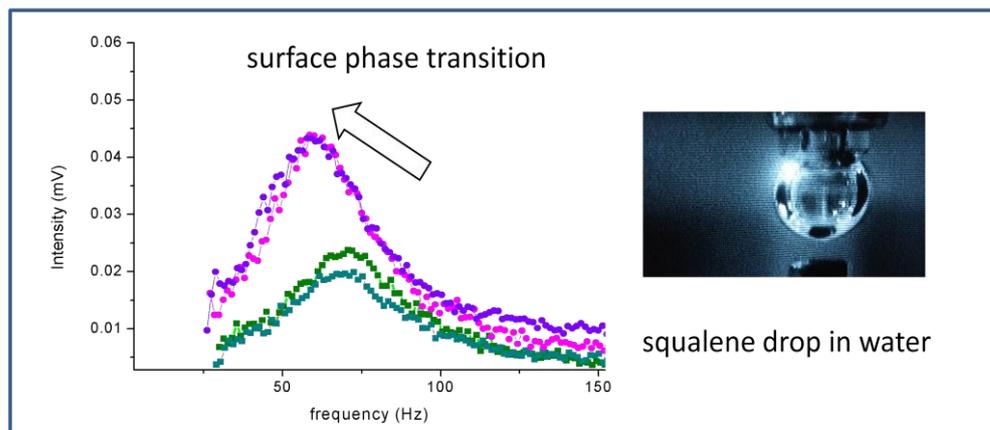


Figure 1 Resonance mode of a 1mm diameter drop of squalene upon addition of minor amount of biosurfactant, undergoing gas to liquid phase transition of the interface monolayer.

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# Structural evolution of POPC/POPE supported lipid bilayers intercalated with quantum dots

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The development of nanocomposite materials for the delivery of therapeutic agents has introduced new opportunities for improved medical treatment. In particular, quantum dots (QDs) as components of functional systems are promising for medical imaging, theranostics, targeted therapy, drug delivery and biosensing. Increasing use of QDs in biological applications motivates exploration of their physical interactions with biological systems, particularly the cell membrane. However, little is known about the influence of internalized QDs on supported lipid bilayer physicochemical properties, or how the bilayer lipid composition affects QD stability inside the bilayer. Furthermore, understanding of the effect of QD sizes on the structure of lipid membranes is important to assessing the viability of their biological applications and potential cytotoxicity.

The main goal of the presented study was to characterize the structure (such as thickness, roughness and density) of supported POPC/POPE lipid bilayers containing hydrophobic cadmium sulphide (CdS) QDs of size ranging from 2.7 nm to 5.4 nm, using *in situ* synchrotron X-ray reflectivity. Complementary Cryo-Transmission Electron Microscopy (cryo-TEM) showed that the CdS QDs were intercalated into the hydrophobic part of lipid bilayer during liposome formation. In addition, fluorimetric emission spectra confirmed the presence of fluorescent QDs within the liposome structure in their phosphate buffered saline (PBS) dispersion. The supported bilayers were obtained by incubating the positively charged polyethylenimine (PEI)-coated silica substrate in QD-intercalated POPC/POPE liposomes in PBS. *In situ* X-ray reflectivity captured the kinetic process of liposome rupturing upon this incubation process. A bilayer structural change as a function of incubation time in the liposome solution was observed, with the bilayer thickness and surface coverage increasing over a period of 1-24 h. The bilayer structure also depended on the CdS QD size. Our results demonstrate that hydrophobic CdS QDs can be successfully embedded into lipid bilayers, and the bilayer formation dynamics and the final bilayer structure depend on the QD size.

**Acknowledgements** The financial support of MCITN NanoS3, CONACYT, and the Erasmus+ programme (project number: 2016-1-PL01-KA103-023786) is acknowledged. XRR was performed at the ESRF XMas beamline, which is a mid-range facility supported by EPSRC. We are grateful to all the beamline team staff for their support.

# In Vivo Protein Corona Formation on Gold Nanoparticles of Various Size and Shape

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Protein corona formation is a well-known process that modifies the identity of nanoparticles upon contact with the biological milieu, thereby affecting their *in vivo* performance. Although most studies are carried out *in vitro*, these conditions do not accurately represent the *in vivo* situation. Our study is thus focused on protein corona formation around gold nanoparticles (AuNPs) *in vivo*. The aim of this research is to achieve a better understanding of how protein corona is influenced by the size and shape of NPs. For this purpose, gold nanorods (AuNRs) and gold nanostars (AuNSts) of 40 and 70 nm of size were intravenously injected in CD-1 mice, recovered by cardiac puncture and then separated from unbound plasma proteins. Physico-chemical characterization of nanoparticles before and after protein corona formation was performed by Dynamic Light Scattering (DLS), UV-Visible Spectroscopy and Transmission Electron Microscopy (TEM). Protein coronas were quantitatively and qualitatively characterized by LC-MS/MS. Our results show that both, size and shape, have an impact on both the amount of adsorbed protein and the composition of the protein corona in the case of *in vivo* corona. This study is expected to open a full method of analysis that is closer to real world applications of nanomedicine.

**Acknowledgements** The financial support of the University of Manchester and CIC biomaGUNE.

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# Interactions in Polyelectrolyte-Surfactant Mixtures

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Mixtures of polyelectrolytes and surfactants are attracting huge interests due to their ubiquitous nature. Polyelectrolytes are soluble in aqueous media, and mostly found in industrial and biological processes associated with neutral or charged surfactant (1). These associations results in the formation of polyelectrolyte-surfactant complexes in the bulk liquid and at fluid-fluid interfaces. Polyelectrolyte-surfactant complexes adsorb at liquid-air interface to form thick layer which enhances stability in systems such as foams. The adsorption of the complexes and surfactant at the interface modifies the tension at the surface and the response of the surface to shear and compression stresses. Dilational elasticity gives a measure of the surface resistance to compression or expansion (2).

In this work, I have employed three (3) tensiometric techniques to study the adsorption behavior of PDADMAC-SLES mixtures at the air-water interface. In addition, the surface dilational elasticity and viscosity of the mixtures in a wide frequency range (0.01Hz-1kHz) has been measured by combining the Oscillating Barriers (OB) and Electrocapillary Wave (ECW) techniques. The binding behavior of the SLES to the PDADMAC was studied by constructing a binding isotherm.

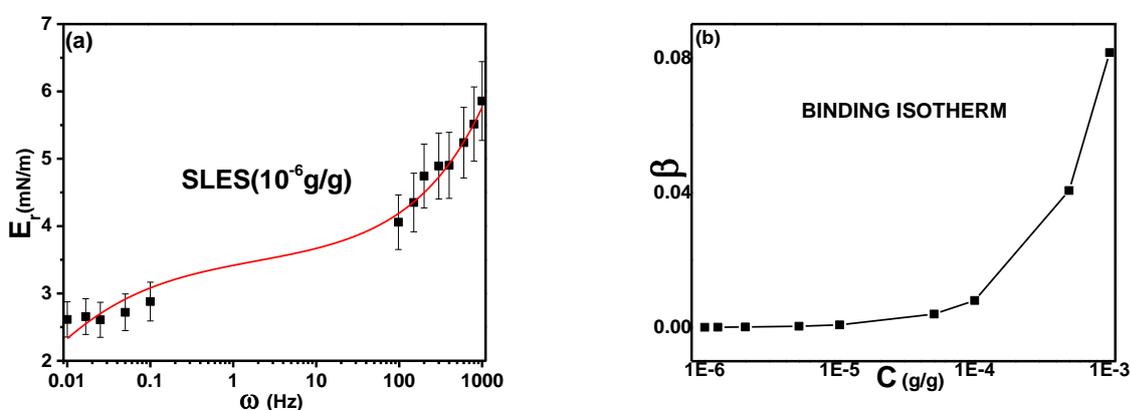


Figure (a) Surface Dilational Modulus of SLES ( $C=10^{-6}$ g/g) and (b) Binding Isotherm of PDADMAC+SLES

The binding isotherm indicates that the SLES was completely bound to the PDADMAC for all concentrations of SLES studied.

**Acknowledgements** The financial support of Marie Curie ITN is highly appreciated.

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# Oligonucleotide sensor based on selective capture of upconversion nanoparticles triggered by target-induced DNA inter-strand ligand - reaction.

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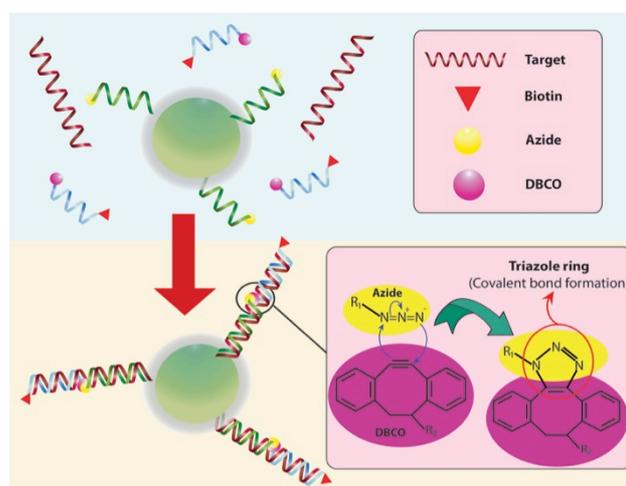
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Short non-coding oligonucleotides, such as microRNAs, are gaining interest as potential biomarkers for early diagnosis of different conditions like cancer, Alzheimer disease or even viral infections.<sup>1</sup> However, the small size of these sequences makes challenging the design of probes for their detection, as this implies that the duplexes formed upon hybridization are relatively unstable.<sup>2</sup> This hampers the sensitivity of the detection assays, as it is necessary to use low-stringency washes in order to avoid dehybridization of the complexes. In this work, a sensor based on click-chemistry and upconverting nanoparticles (UCNPs) as labels, has been developed. Two probes are used for the detection of a target sequence: one is covalently attached to the UCNPs' surface, and contains an Azide group (-N<sub>3</sub>), while the other one is free in solution and contains a DBCO and a biotin modification. When the target is present the two probes hybridize, permitting the formation of a covalent bond between the -N<sub>3</sub> group of one probe and the DBCO of the other (Figure). After capturing the resulting covalently biotinylated UCNPs in Streptavidin (SA) coated wells, it was possible to apply harsh washes to reduce background noise, which in turn permitted to achieve a limit of detection of 100 fM.

**Figure** Scheme of the detection mechanism: When the target sequence is present, the probe containing the N<sub>3</sub> (Azide) group and the probe containing the DBCO modification face each other. At this point the "click" reaction takes place, yielding a covalent bond between both probes upon a triazole ring formation.



**Acknowledgements** The authors are grateful for the financial support from the Bill & Melinda Gates Foundation, with Grant OPP1128411, Asociación Española Contra el Cancer, Santander-Universidad Complutense project PR26/16-12B-3, and from the Spanish MINECO for the projects MAT2014-55065-R, SAF2014-56763-R, and FIS2013-41709-P.

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# Glassy orientational dynamics in plastic crystals of aspheric colloids

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Aspheric molecular or colloidal systems, with only a slight degree of anisotropy, often assemble into plastic crystals [1]. While plastic crystals exhibit the full positional order of a crystal, particles can freely rotate around their centers of mass, rendering them orientationally disordered.

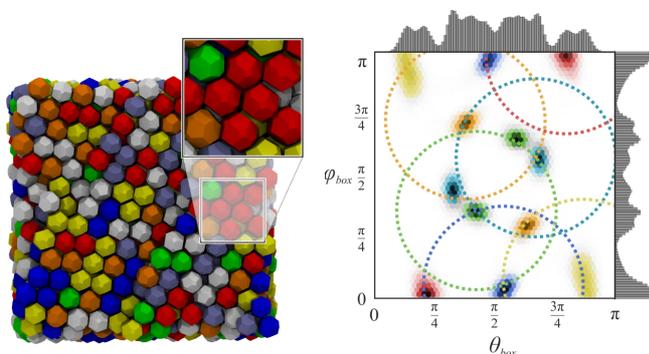
In this work [2], we study the self-assembly process of truncated-hexbipyramid-shaped effectively hard Bi-nanocrystals in experiment and simulation and present evidence of glassy orientational dynamics in the plastic phase of this system.

Experimentally, we assembled the Bi-nanocrystal super-structure through diffusion of a non-solvent into colloidal nanocrystal suspension and studied the crystallisation process with small angle x-ray scattering (SAXS). To model the self assembly process in simulation, we used NPT Monte-Carlo.

At intermediate packing fractions, in experiment as well as in simulation, we find that the system assembles into a plastic-fcc crystal, as expected. However, this so-called plastic crystal is not orientationally isotropic: Instead, six distinct orientations are taken on more frequently and, with increasing packing fraction, all particles assume one of these six global orientations.

Upon increasing the pressure further, we find that, instead of transitioning into the more stable, parallelly aligned crystal, the system exhibits glassy behaviour. Reorientations remain possible, but occur in large orientational jumps, leading into one of the six global orientations.

We argue that glassy orientational dynamics upon freezing may not be unique to truncated hexbipyramids, but it might be a general feature of polyhedral plastic crystals. Hence, we hope that this work will inspire more research on the general properties of plastic-crystal to crystal transitions.



**Figure 1** The plastic crystalline state with 6 global orientations (particles in color). Left: simulation snapshot. Right: Distribution of particle orientations with respect to one simulation box vector.

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# Formation of oriented plasmonic oligomers on elastomeric substrate via macroscopic strain

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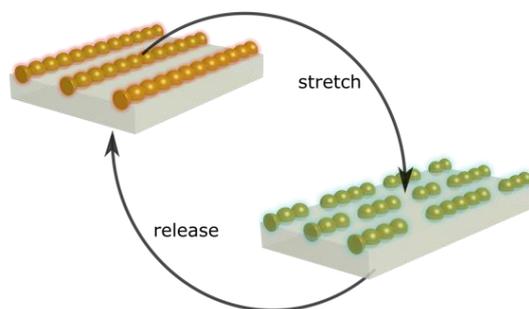
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We present the formation of oriented chains of few plasmonic nanoparticles, so called plasmonic oligomers, by controlled fragmentation of linear particle assemblies [1] into finite sub-chains. Detailed investigations of the fragmentation process are conducted by in-situ atomic force microscopy (AFM) and correlated to UV-vis-NIR spectroscopy. [2]

By evaluation of the strain dependent optical properties we found a reversible, non-linear shift of the dominant plasmonic resonance. These measured optical properties were analyzed by deconvolution for the corresponding ensemble of oligomers by electromagnetic modeling and compared to the oligomer length distribution and dispersity yielded from the AFM measurements. Based on these results and mechanical modeling (lattice spring method), we prove a formation mechanism which provides experimental guiding lines. Following this strain-dependent fragmentation mechanism the chain length can be controlled depending on the ratio of cohesion between the particles and adhesion of the colloids to the supporting elastomeric substrate.

We demonstrate, that mechanical stimulus is a powerful tool for the scalable fabrication of oriented linear plasmonic oligomers and opens new avenues for strain-dependent optical devices and mechanoplasmonic applications. As an example, for surface-enhanced sensing, the reversible switching of the nanostructure may be utilized to trap/infiltrate target molecules into uniform hot-spots



**Figure 1:** Reversible fragmentation of quasi-infinite gold nanoparticle chains into defined oligomers, induced by macroscopic strain

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[2] Anja Maria Steiner et al. *manuscript submitted*

# Preparation and Light Scattering Properties of Hollow Silica Nanocubes

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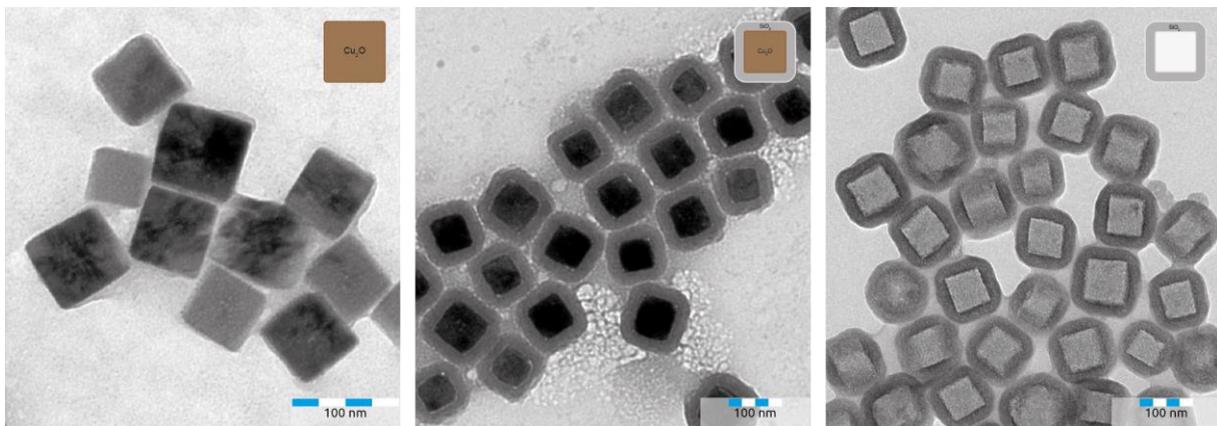
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Recently it was shown that hollow micron sized silica cuboids can form dense colloidal crystals, either due to gravitation [1] or, by the depletion effect from non-adsorbing polymers [2]. The crystal structures turn out to be highly sensitive to the shape details (cube-ness/curvature) of the colloids. Here we report a new preparation method for hollow silica nanocubes, with sizes and shapes that could not be accessed with the hematite based approach [1,2]. By using cuprous oxide ( $\text{Cu}_2\text{O}$ ) nanocubes as a sacrificial template, hollow silica nanocubes can be obtained, with edge lengths ranging from 50 – 150 nanometer and are characterized by a shape parameter between 3 – 6.

The new hollow silica colloids are, in contrast to the large, rapidly, sedimenting cubes from ref [1,2], very suitable for light scattering studies. Results will be presented on form factors and optical contrast variation for single cubes, and the first structure factors from static light scattering by optically matched concentrated cube fluids.



**Figure 1:** Left:  $\text{Cu}_2\text{O}$  nanocubes, Middle:  $\text{Cu}_2\text{O}@\text{SiO}_2$  core-shell nanocubes, Right: Hollow Silica Nanocubes.

**Acknowledgements:** This research is supported by the NWO Domain Applied and Engineering Sciences and DSM Advanced Surfaces.

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# Magnetically separable polymer/metal oxide nanocarriers prepared in miniemulsion with high performance in heterogeneous catalysis

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Heterogeneous catalysts are nowadays widely applied in many industrially relevant reactions because of the economic, technical, and environmental advantages with respect to homogeneous analogues. The immobilization of catalytically active components within a polymeric matrix, acting as supporting material, is a convenient pathway to overcome drawbacks of homogeneous catalysis in terms of separation and recyclability of the catalyst. In addition, the incorporation of a magneto-responsive component allows the recovery of the catalyst by the application of an external magnetic field, which avoids the need of time and energy demanding separation operations. The introduction of magnetic functionalities is also very attractive for applications in biomedicine.

This work is focused on the preparation of magnetically separable hybrid polymer/metal oxide nanocarriers with high performance in heterogeneous catalysis. Magneto-responsive nanoparticles ( $\text{Fe}_3\text{O}_4$ ) and catalytically active units, represented either by metal oxide nanoparticles ( $\text{TiO}_2$  and  $\text{CeO}_2$ ) or proline-based chiral monomers, have been successfully incorporated into a polymer matrix. Among other colloidal methods, miniemulsion was chosen as a versatile synthetic platform that allows the preparation of hybrid nanostructures (nanoparticles or capsules) with controlled morphology via different strategies: miniemulsion polymerization [1], inorganic crystallization [2] or interfacial polymerization [3].

The selective migration of the aimed functionalities within the supporting matrix has been addressed by tuning the hydrophobicity of the functional units. For this purpose, the surface functionalization of the inorganic components was performed via silane chemistry [1] and a specific structural design and synthesis of chiral monomers was developed [4]. As a result, we have prepared hybrid nanostructures with a catalytic functionality, accessible on the surface of either polymer nanoparticles with a magnetic core or capsules with a liquid core surrounded by a magnetic–polymer shell. The performance of the final material in terms of heterogeneous catalysis was tested for different model systems. Also the encapsulation and controlled release of dyes from the nanocontainers was studied.

In summary, we present the design and development of multifunctional hybrid nanocarriers, magnetically separable and highly performing in heterogeneous catalysis. The desired properties of the complex multifunctional nanostructures result from the morphological control reached by different strategies in miniemulsion based on a common principle: the tuning of the interfacial chemistry involved.

**Acknowledgements** The authors thank the Max Planck Society and the Spanish Ministry of Economy, Industry and Competitiveness (Ramón y Cajal grant to R.M.E., grant no. RYC-2013-13451) for financial support.

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# Upconverting nanoplatform for shifting metallodrugs light activation in the therapeutic window

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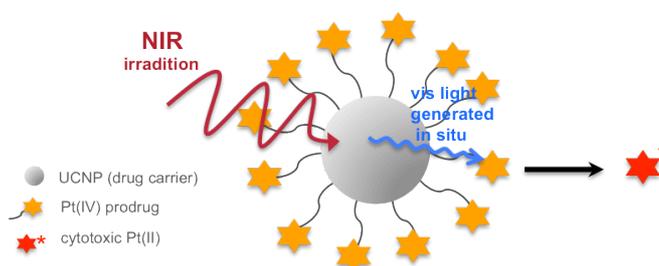
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Light-activated therapy is attracting much of attention because it provides a solution for the major drawback of current cancer therapy, i.e. the lack of spatial selectivity, resulting in unwanted toxic effects and lower treatment efficacy.

In recent years light-activatable Pt(IV) complexes with encouraging antitumor properties have been developed and investigated for photo-activated chemotherapy (PACT). These complexes owe their activity to their capacity to generate biologically active species in situ with high spatiotemporal control when photoactivated with visible light.<sup>1</sup> However, maximal light penetration into tissues (up to 1 cm) with minimal damage to biological components is achieved only in the therapeutic window of the red and near-infrared (NIR) spectrum ( $\lambda$  in the range 600–1000 nm), where these complexes usually exhibit poor absorption properties thus limiting their clinical applications.

Aiming to overcome such limitations, we have recently explored the use of upconverting nanoparticles (UCNPs) as carriers and phototriggers for the NIR photoactivation of anticancer Pt(IV)-complexes.<sup>2</sup> UCNPs, made of an optically inert host matrix doped with optically active lanthanide ions, (NaGdF<sub>4</sub>: Yb, Er(or Tm) can convert highly tissue-penetrating NIR light ( $\lambda$ =980 nm) into UV/vis/NIR light via a multiphoton process. Conveniently, the higher energy photons emitted by UCNPs upon NIR-light excitation can activate a light-sensitive prodrug attached to the UCNPs, leading to the release of an active anticancer agent (Figure 1).

This contribution concerns the synthesis of appropriate UCNPs and their functionalization with highly photosensitive diiodido-Pt(IV) diamine complexes. Two different strategies of attachment of Pt(IV)-complexes were exploited. The effect of NIR light on the release of Pt(II) cytotoxic species was investigated as well as the binding of released Pt to DNA in a model system. Finally, the cytotoxic actions of such modified UCNPs on human leukemia cancer cells, with and without irradiation with NIR light, have been investigated.



**Figure 1.** Sketch of mechanism of photoactivation of Pt(IV)-complex by near-infrared (NIR) radiation.

**Acknowledgements.** This work was partially funded by European Research Council (BioIncmcd 247450), Italian MIUR (FIRB RINAME RBAP114AMK) and HORIZON2020 (Partial-PGMs 686086).

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# PFA-PEG particles: A colloidal model system for the investigation of phase diagrams of PEGylated drug carrier systems

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Pegylated particles like proteins, peptides and lipid- or polymer-based nanoparticles are known as potential drug delivery systems (DDS) or as nano drug carriers (NDC) [1,2]. Their potential as therapeutic agents for highly specific while also highly vulnerable substances leads to an increased use of PEGylated particulate materials in modern pharmaceutical technology [3]. Current research deals with e.g. completely new systems [4], shape effects [5] or the influence of the PEG density on the biocompatibility [6]. However, the phase behaviour of the DDS is not really covered. This can pose severe problems for larger therapeutic molecules with a low carrying ratio of the DDS. Due to the unknown behaviour at higher concentrations most of the DDS are administered via injection into the blood stream in high dilution. As a consequence the potency of the drug shrinks with lower carrying ratios of the DDS [2]. As a result higher concentrations or different formylations are needed but difficult to achieve without detailed knowledge of the DDS phase behaviour.

In an attempt to close this gap we synthesised a new model system, consisting of a highly fluorinated core and a sterically stabilizing PEG-shell [7]. The main advantage of this model system over standard PEG-DDS model systems [8] is that their phase behaviour can be easily investigated via light scattering by using an aqueous solvent and thereby avoiding multiple scattering effects, i.e. sample turbidity, at high concentrations. Based on a simple emulsion polymerisation technique the overall size of the particles, the thickness of the PEG-layer and even the PEG-chains of the stabilizing layer can be easily varied.

With these particles and different light scattering techniques as well as other complementary techniques such as microscopy and rheology, we gained first insights into the phase behaviour of PEGylated particles. Our findings can lead to higher concentrated carrier systems without unwanted inter particle interference and new formylations e.g. gels or cremes.

**Acknowledgements** The financial support of the DFG through the IRTG: Soft Matter Science project C1 is gratefully acknowledged.

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# Core-doped nano-radiomaterials for Enhanced Molecular Imaging

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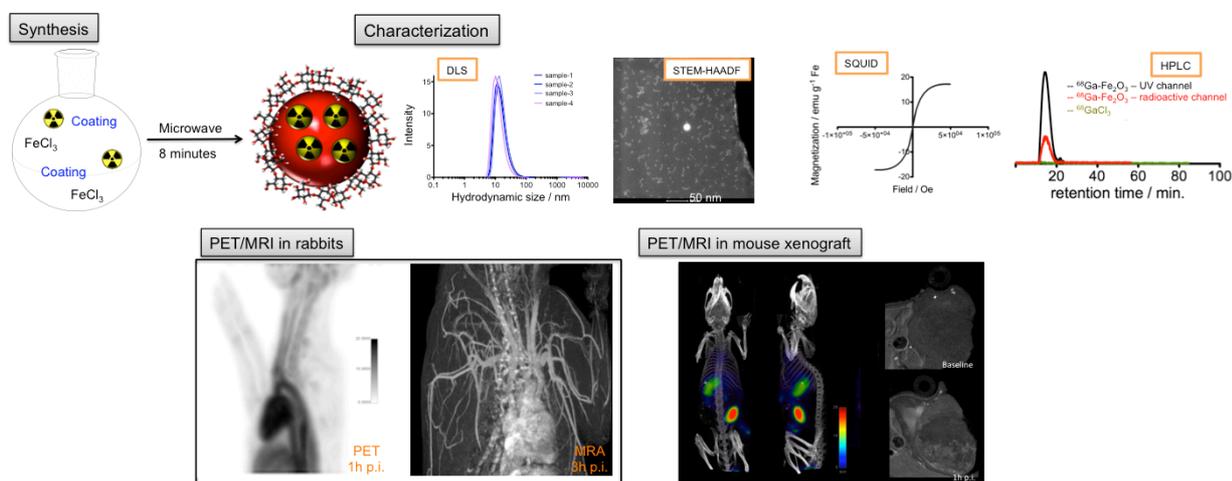
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The use of nano-radiomaterials for multimodal imaging is particularly appealing due to their size-dependent features with hybrid PET/MRI as one of the most promising approaches. Here, we describe the synthesis and *in vivo* use of extremely small, radioisotope core-doped iron oxide colloids, using as examples <sup>68</sup>Ga or <sup>89</sup>Zr. Microwave-driven synthesis was carried out to produce extremely small particles in 8 min and with different isotopes in the crystalline structure of the colloid. After purification by gel filtration chromatography, their physicochemical properties, *in vitro* toxicity and *in vivo* features were studied.<sup>1-3</sup> This approach yielded very small particles with a core size of  $2.1 \pm 0.2$  nm and hydrodynamic size of  $18.2 \pm 2.5$  nm. They show large  $r_1$  values enabling positive contrast in MRI. The activity incorporated for <sup>68</sup>Ga or <sup>89</sup>Zr was also highly reproducible. The utility of these particles for *in vivo* positive contrast MRI was first investigated in rabbits, by injecting cold nanoparticles at a low dose into healthy animals. The short  $T_1$  relaxation time produces high signal intensity in MR angiographic (MRA) acquisitions and the integrated radioisotope allowed detailed imaging of vessels by PET. Further surface biofunctionalisation allowed for *in vivo* PET/MRI detection of angiogenesis with one single administration of our probe. These particles can be used for a wide range of applications, from angiography to targeted imaging with the covalent attachment of different biomolecules and pretargeted molecular imaging, examples on these will be shown.



**Figure 1.** Synthesis, characterization and *in vivo* applications of core-doped nano-radiomaterials.

**Acknowledgements** The financial support of Spanish Ministry of Economy (MINECO, SAF2016-79593-P) and Instituto de Salud Carlos III (DTS16/00059).

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# Combination of Layer-by-Layer based Drug Delivery Systems and Vesicular Stomatitis Virus G-protein for Enhanced Intracellular Processing of Active Agents

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The development of both new therapeutics and novel drug delivery systems is an essential requirement for the efficient therapy of an increasing number of diseases. New delivery systems must consider biodegradability, protective packaging and targeted and controlled release for efficient delivery. One approach for an efficient drug delivery into the respective target side of cells that fulfills these requirements is given by Layer-by-Layer (LbL) based microcarriers due to their modularity and high multi-functionality. Biopolymers with opposite charge are self-assembled on a spherical template and then equipped with an outermost lipid bilayer, leading to an enhanced biocompatibility and cellular uptake by *e.g.*, specific antibody binding [2].

Despite intensive efforts, the specific intracellular transport of most conventional drug delivery systems, including LbL microcarriers, still appears to be a challenge. Often, they are retained and eliminated in the phagolysosomes of cells [1]. To overcome this problem, we are using virus-functionalized LbL microcarriers for an improved intracellular drug delivery into the cytoplasm of cells. Here, the lipid bilayer covering the microcarriers will serve as a platform for the incorporation of virus particles, which have evolved a machinery optimized for efficient cellular uptake and the subsequent release of their genetic information into the cell. The fusion protein (VSV-G) of the virus, which is localized on its surface, unfolds in presence of acidic pH and induces fusion with any present membrane [3]. Thus it can be utilized for the fusion of the virus with the lipid membrane on the LbL microcarrier and the subsequent fusion of the virus-functionalized LbL microcarriers with the endosomal membrane of the cells. In our study we used Vesicular Stomatitis Virus (VSV) as a model virus. We could demonstrate that VSV interacts and fuses with the lipid-bilayer equipped LbL microcarriers. The presence of the VSV-G and viral RNA on the surface of the LbL microcarriers was detected by fluorescence markers and analyzed by confocal microscopy and flow cytometry.

This new delivery system will offer many advantages including the transport efficiency of active agents into the cytoplasm will be considerably enhanced.

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# Interlocking of two Drug Delivery Systems: Layer-by-Layer Microcarriers and DNA Origami Nanocarriers

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Smart and structured drug delivery systems offer a promising approach in enhanced transport of active agents. To improve their protection during transport as well as the specific release, our investigations focus on the combination of autonomous drug delivery systems: DNA origami nanocarriers and Layer-by-Layer (LbL) microcarriers will be interlocked in order to utilize their specific advantages.

The adjustable properties of the micrometer sized modularly built LbL carriers provide a firm base for advanced modification. Different core and shell materials, the stepwise assembly of biopolymers forming a multilayer as well as the subsequent high potential of integrating different kinds of molecules or nanoparticles into multilayer or core makes this system very versatile. [1] Contrary to the LbL shell, the nanometer sized DNA origami provides an encapsulated package of the agent leading to a protected transport. Tunable release mechanism can further be achieved by the controllable opening of an attached lid. [2]

In our investigations we demonstrate the successful adsorption of DNA origami nanocarriers onto biopolymer coated microcarriers with good long-term stability at variable layer depth. In this context, a high coating yield of LbL microcarriers with DNA origami has been obtained while their nanostructure remains unaltered during assembly and storage. First approaches of trapping biomolecules in the 13 nm × 13 nm × 40 nm cavities of the origami illustrate the applicability as a sequential drug delivery system.

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# Thermosensitive polynorbornene poly(ethylene oxide) nanoparticles loaded with miDNAs : an innovative approach for acting on cancer-associated pain

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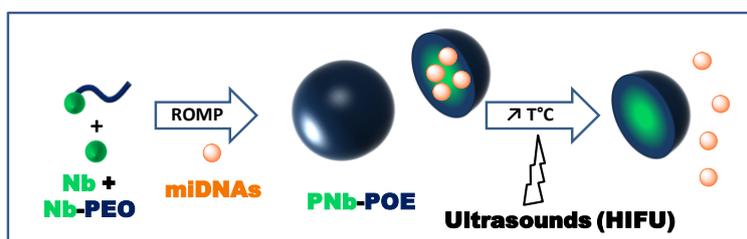
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miDNAs have been recently identified as a novel class of therapeutic tools for acting on the cancer-associated pain. Polymeric nanoparticles (NPs) are an interesting way to trap and protect such molecules to allow their transport through the bloodstream to the spinal cord. In this project, we propose to synthesize core/shell NPs having an hydrophobic polynorbornene core and an hydrophilic poly(ethylene oxide) shell [1]. The use of the poly(ethylene oxide) shell allows the furtivity of the NPs and enhances the NPs circulating half-life. These NPs are obtained by Ring-Opening Metathesis coPolymerization (ROMP) of norbornene with an  $\alpha$ -norbornenyl-poly(ethylene oxide) macromonomer in dispersion. The norbornene and the macromonomer are both soluble in the solvent media. The formed polynorbornene, which is insoluble, precipitate and is stabilized by the poly(ethylene oxide) chains to form spherical NPs with diameters around 350 nm. The introduction of miDNAs at the beginning of the reaction allows their trapping inside the NPs.

After the crossing of the blood-brain barrier by the NPs, the miDNAs molecules would be released through a temperature increase by using high intensity focused ultrasounds (HIFU technology). This phenomenon is possible thanks to a glass transition of the polynorbornene around 35°C, close to the physiological temperature. A temperature increase higher than the glass temperature involves an increase of the mobility of the hydrophobic polymer chains which implies a contraction of the NPs core and the release of the miDNAs molecules [2].

In this contribution will be presented the influence of the chemistry ([monomer]/[macromonomer], adding of a cross-linker, functionalization of the PEO chains) on the entrapping rates and the release kinetics of the active molecules. The miDNAs releases as a function of the time and the temperature have been monitored by UV/visible spectroscopy. We also will show the limitation of the uncontrolled miDNAs release by modulating the rigidity of the polynorbornene core of the NPs and by introducing functional groups at the  $\omega$ -end of the PEO chains. Finally, we will prove the ability of the NPs to cross the blood-brain barrier after its opening by HIFU with *in vivo* tests on mice by using Rhodamine labeled NPs [3].



**Figure 1** Synthesis of thermosensitive NPs loaded with miDNAs and release of the active molecules

**Acknowledgements** Authors would like to thanks the French Institut National du Cancer (INCa) for the financial support.

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# Synthesis and characterization of iodinated polymer particles and use as a contrast agent for tomography using a spectral scanner

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Contrary to conventional Computed Tomography (CT) that provide a single attenuation measurement, Dual Energy scanners (two attenuations at different energy ranges) and recently prototypes of Spectral Photon Counting CT (SPCCT), can discriminate between different elements by recording the energy spectrum that passes through the tissues at each voxel of the image. This allows material decomposition that provides quantitative determination of the concentration of a specific element. Iodine-based materials are widely used and efficient contrast agents for CT scanners. Contrast agents in the form of nanoparticles that specifically bind to the tissue to be imaged, provide contrast enhancement in respect to small molecules. The purpose of this study is to combine the SPCCT technology and contrast agents as nanoparticles. In order to do so, iodinated polymer nanoparticles were designed, to be used as contrast agents for the SPCCT.

The iodinated polymer material was prepared by covalently linking an iodinated molecule onto Poly (vinyl alcohol) (PVAL 13 kDa) (Figure 1). The radiopaque moieties were successfully incorporated onto the polymer and the grafting rate (degree of substitution, DS), calculated from the <sup>1</sup>H NMR spectrum, was over 50 mol%. The iodine content determined from the DS was over 70 wt%. Elemental analysis for iodine content confirmed these results.

Nanoparticles of iodinated polymers were prepared using the Nano-precipitation method. Dynamic Light Scattering (DLS) and Cryogenic Transmission Electron Microscopy (Cryo-TEM) measured particle size. Nanoparticles were stable and well-separated (Figure 2) and their mean diameter was in the 40 – 200 nm range, depending on the concentration of polymer.

Radio-opacity of the contrast agents and sensitivity of the scanner for iodine were evaluated in-vitro on phantoms prepared with suspensions of contrast agents at different concentrations (Figure 3). Bio-distribution was studied in-vivo by experiments performed on small animals (intravenous injections to rabbits). Such measurements were performed on a conventional CT and on the SPCCT for the sake of comparison.

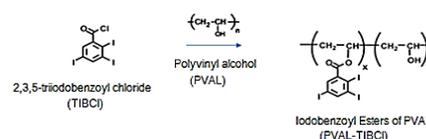


Figure 1. Iodinated polymer synthesis: covalent linkage of 2,3,5-triiodobenzoic chloride onto

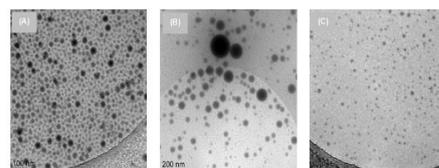


Figure 2. Cryo-TEM images of dispersions of iodinate polymer in water at different concentrations JB43 and JB48 (A & B) and block co-polymer PCL-b-PEG micelles (C).



Figure 3. Phantoms prepared with suspensions of iodinated polymer in water at different concentration. (JB48).

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# Investigating the Morphology of Polymer Thin Films and Nanostructures on Mica and Graphite Surfaces

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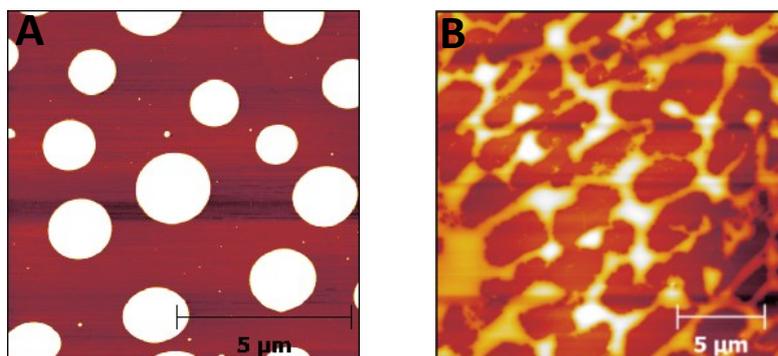
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In order to promote the intelligent design and manufacture of composite materials, it is essential to understand and control the behaviour of polymers in the vicinity of a surface. The bulk physiochemical properties of composite materials can be heavily influenced by the fundamental interactions between their polymer matrix and filler components [1]. Despite this, the behaviour of polymers at a surface is often poorly understood at the nanoscale, as bulk behaviour can be very different when compared to behaviour at an interface [2].

To investigate this, we studied the morphology of poly(styrene-co-butadiene) random copolymer thin films and nanostructures on mica and graphite surfaces. The experiments were prepared at various solution concentrations and molecular weights. Atomic force microscopy was used to image the surfaces at the nanoscale. Our results show that at lower concentrations, surface effects are dominant causing the polymer behaviour to be very different on each surface. On the mica surface, weak adsorption creates spherical-cap shaped nanodroplets. On the graphite surface, there is much stronger adsorption, and polymer morphology is extremely variable forming continuous networks, asymmetrical aggregates, and epitaxy-like structures. At higher concentrations, bulk effects dominate and the polymer behaviour on each surface is very similar as ultrathin films form with some dewetting taking place. On the mica surface, the contact angle of the nanodroplets are highly dependent on droplet size and a distinct minimum occurs at a droplet radius of 100 – 250 nm. This is due to an increased elastic modulus of smaller droplets, and the influence from surface heterogeneities for larger droplets. On the graphite surface, the contact angles of the polymer aggregates are independent of droplet size due to stronger polymer/surface interactions. We have provided an insight into the fundamental behavior of a polymer on two different surfaces; showing both distinct similarities and differences in the morphology and contact angles of the polymer structures.



**Figure 1** AFM height images showing poly(styrene-co-butadiene) random copolymers with a molecular weight of 86 kg/mol and a solution concentration of 3.71 mg/ml deposited on: (A) a mica surface and (B) a graphite surface.

**Acknowledgements** We acknowledge the EPSRC and the SOFI CDT for financial support.

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# Enhancing carbon dioxide capture using robust superomniphobic membranes

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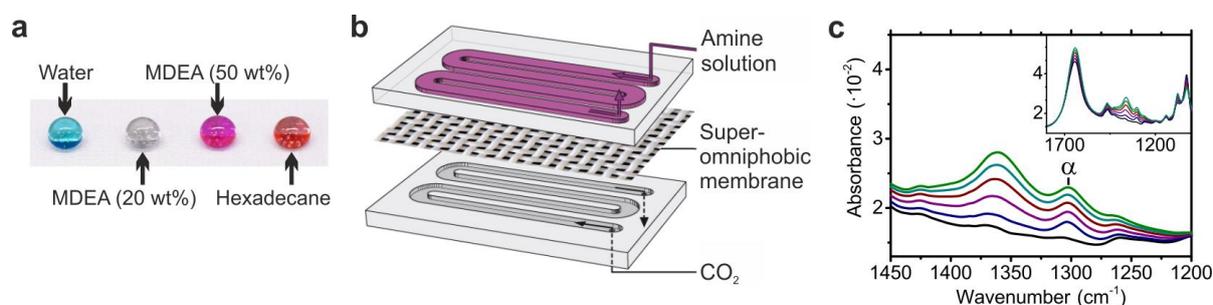
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Limiting carbon dioxide (CO<sub>2</sub>) emission into the atmosphere to reduce global warming is a major issue of our times. However, CO<sub>2</sub> capture is still highly challenging and energy consuming. Therefore, more efficient techniques are required [1,2].

Here, we introduce superomniphobic membranes for efficient post-combustion CO<sub>2</sub> capture. In a gas contactor membrane system, a membrane spatially separates the gas and liquid streams. The flue gas is pumped across one side of the membrane and the capture solution across the other. Unique to our superomniphobic membranes is that the capture liquid stays on the top-most part of the membrane, preventing wetting of the membrane. Wetting of the pores greatly reduces the efficiency of CO<sub>2</sub> diffusion through the membrane into the capture solution. To fabricate mechanically, chemically and thermally robust superomniphobic membranes, we coated polyester fabrics with silicone nanofilaments. Subsequent fluorination renders them super liquid-repellent even against concentrated amine solutions, which are most commonly used for CO<sub>2</sub> capture in industry and academia. The uptake of CO<sub>2</sub> in the capture medium, here a concentrated N-methyldiethanolamine (MDEA) solution, was monitored by infrared spectroscopy. The CO<sub>2</sub> capture rates of our superomniphobic membranes were enhanced by up to 40% compared to state-of-the-art commercial membranes and remained unaltered within 50 hours of operation.

We anticipate that this new design principle will stimulate the development of the next generation of highly efficient gas contactor membranes [3,4].



**Figure 1** a) Photograph of 15 µL drops (stained) of water, aqueous MDEA solutions (20 wt% and 50 wt%) and hexadecane on a superomniphobic membrane. b) Sketch illustrating the CO<sub>2</sub> exchange setup including the ATR-FTIR spectrometer. c) Time evolution of FTIR spectrum of MDEA solution (20 wt%) over 60 min CO<sub>2</sub> gas exchange through a superomniphobic membrane.

**Acknowledgements** The financial support of ERC Advanced Grant 340391-SUPRO, COST MP1106 and by the German Research Foundation (DFG) within the Collaborative Research Centre 1194.

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# Liquid drop motion through shear forces on a smooth rigid substrate

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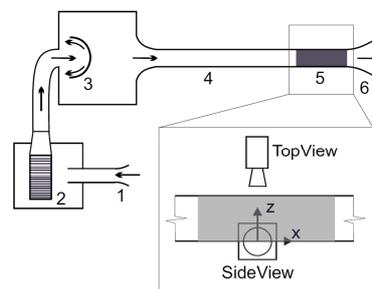
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Liquid drop motion driven by shear forces on a smooth rigid substrate is a phenomenon relevant to various applications, e.g. process engineering, multiphase transport, printing as well as ice accretion or vehicle soiling<sup>1</sup>. Various forces associated with substrate wettability, viscosity in the drop or aerodynamic drag play an essential role in determining drop motion on the wall. Estimation of the conditions for inception of motion and the drop translational velocity is a challenging task, since the problem is time dependent and three-dimensional. An extensive basis of experimental data is needed in order to better understand the physics behind this phenomenon. This is the main subject of the present study.

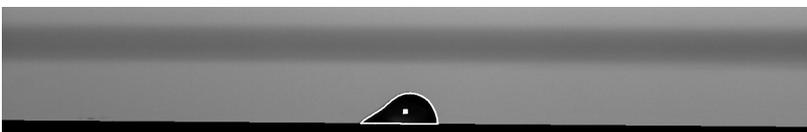
The phenomenon of shear driven flow of a drop is investigated in a wind channel. In order to keep the aerodynamic shear forces on the drop constant in the streamwise direction a fully developed turbulent, two-dimensional Hagen-Poiseuille flow<sup>2</sup> is used. A water drop is placed on a smooth rigid substrate which forms the floor of the channel and the drop motion is visualized using a high-speed video system. The apparent contact angles as well as actual drop geometry are determined for each time step and quantified using image analysis algorithms<sup>3</sup>. The drop motion is characterized for varying parameters: drop volume, air flow velocity as well as surface wettability. Finally a semi-empirical model for the drop velocity as a function of the air shear forces is developed.



**Figure 1** Photograph of the experimental setup with the wind tunnel.



**Figure 2** Wind tunnel sketch with the main components: 1 entrance nozzle; 2 radial blower; 3 settling chamber with baffle; 4 flow development section; 5 test section; 6 diffuser.



**Figure 3** Side view image with center of mass and boundaries of a 5  $\mu\text{l}$  water drop. The static advancing and receding contact angles are  $88^\circ$  and  $61^\circ$ . The Reynolds number of the air flow is  $Re_H = 16925$ .

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# Mapping the 2D organization of microgels at liquid interfaces: model surfaces and emulsions

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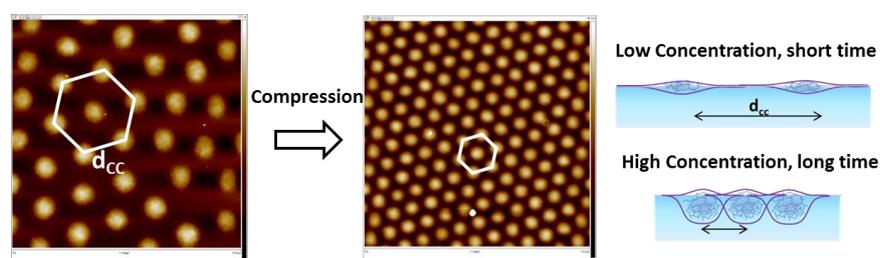
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Microgels are water-swollen cross-linked polymeric particles, which have the ability to change their swelling ratio upon various stimuli. Some of them, such as poly(N-isopropylacrylamide) (pNIPAM), are amphiphilic and adsorb at a liquid interface. pNIPAM microgels have been found to stabilize Pickering emulsions [1] or foam films [2] in good solvent conditions. However, due to their softness, these deformable particles can adopt various conformations at the liquid interface, which has consequences on the macroscopic properties of the resulting emulsions [3].

In the present work, we aim at understanding the properties of the microgels adsorbed at a flat interface, either in spontaneous adsorption [4] or under compression [4, 5]. We study more or less rigid charged and neutral pNIPAM microgels, in various aqueous environments (pH, electrolyte concentrations), at both air-water and oil-water interfaces. Their two-dimensional phase diagram under compression is studied via the Langmuir technique, followed by transfer onto a solid substrate at different surface pressures. The transfer gives an accurate replica of the organization at the air-water interface. The microgels adopt different conformations at the interface and form highly ordered hexagonal lattices on the solid substrate over large areas, with a unique lattice parameter which decreases continuously as the surface pressure increases (Figure 1). We discuss the role of the softness and the structure of microgels on their organization, as well as the contribution of electrostatic interactions.

In emulsions and foam films, the microgels were locked into various conformations, which depended on their kinetics of adsorption at the interface and processing conditions. Mapping the organization versus surface pressure gives clear insights into the state that is reached in dynamics. Taking into account this dynamics into the choice of emulsification pathway leads to the preparation of controlled drops. A broad range of drop sizes can be achieved using high energy methods as well as microfluidics.



**Figure 1** AFM images of microgels ( $10 \times 10 \mu\text{m}^2$ ) transferred on solid substrate after being compressed at the air-water interface and scheme of their profile view in the different conformations.

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# Short Pulsed Laser Micro/Nanostructuring of Surfaces for Improved Functional Applications

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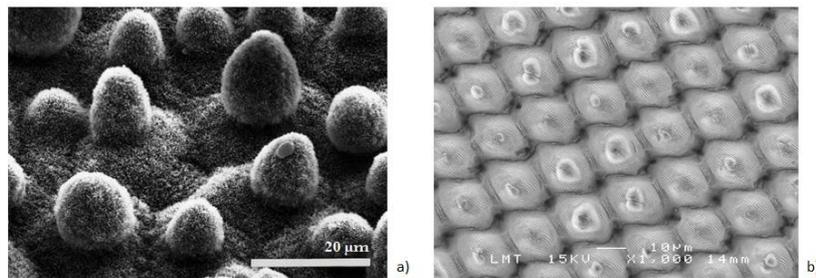
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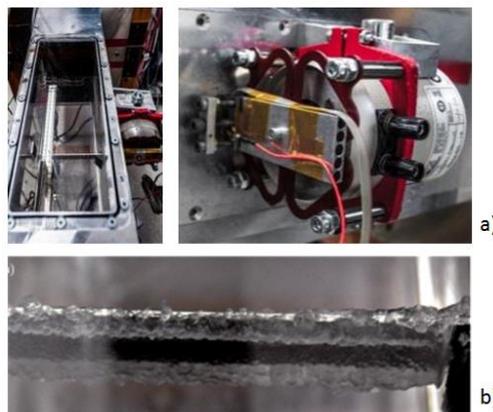
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Ice accretion on aerodynamic surfaces impacts safety and performances of an aircraft. Expensive and not-environmental friendly methods have been used to prevent and control ice formation on-ground (e.g. de-icing fluids) and in-flight (active ice protection systems, e.g. bleed air, mechanical boots). The development of novel functional surfaces can enable the decrease of power needed to avoid ice formation (anti-icing mode) and ice buildup (de-icing mode).

In this work we propose short and ultra-short pulsed laser treatments as a technique to enhance the functional properties of alloys commonly used in the aviation industry. The investigated laser technologies can tune the wetting properties of the materials producing Lotus-like superhydrophobic surfaces (Figure 1), due to the micro/nanostructures generated on them. Ice adhesion tests (Figure 2) are then performed in order to assess the behavior of the manufactured structures with respect to different icing conditions.



**Figure 1.** a) Lotus leaf surface [1]; b) Laser-Induced Periodic Surface Structures (LIPSS) on Ti-6Al-4V [2].



**Figure 2.** a) Ice adhesion test rig developed at Airbus Group Innovations, Munich; b) beam tested for ice accretion.

**Acknowledgements.** This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 675063. Any work or result described in this deliverable is either genuinely a result of LASER4FUN project. Any other source used for its creation has been properly referenced.

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# How are waterborne wood finishes affected by ambient humidity?

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Water-based coatings represent an important segment of coatings technology and serve as an environmentally friendlier alternative to traditional organic-solvent-based coatings. Effectively, because of legislations implemented worldwide (e.g. REACH, EU) there is an urge to replace solventborne with waterborne coatings. However, the development of waterborne coatings with a similar performance has been revealed as a difficult task [1]. Indeed, although waterborne coatings have already improved considerably, they still would benefit from increased water repellency [2]. In other words, not unexpectedly, waterborne coatings are more susceptible to water present in the environment.

We have a specific interest in waterborne wood finishes. Wood is a natural renewable building material widely applied both indoors and outdoors. However, its performance is highly dependent on the ambient humidity. Wood is a hygroscopic material that expands and contracts based on ambient humidity [3]. Additionally, as the wood moisture content increases so does the possibility of colonization by microorganisms [4]. Thus, the control of the moisture content of wood is critical for its effective use. Typically, wood is protected from moisture related effects by the application of appropriate coatings. As mentioned above, restrictions in the use of volatile organic components are also fostering the use of waterborne wood finishes. Due to the susceptibility of wood to ambient humidity, it is of high importance for its effective use as a building material to understand how waterborne finishes behave at different humidities. Of specific relevance is to develop tools to characterize the effect of humidity on the water content and the mechanical properties of wood finishes.

Here we show that surface techniques like Atomic Force Microscopy and Quartz Crystal Microbalance with Dissipation can be used for these studies. Specifically, they can reveal with high sensitivity the water content and viscoelasticity of wood finishes. We will present data for a variety of finishes based on poly-acrylic acids and poly-urethane dispersions i.e., those more commonly employ in wood applications, and discuss as well the role of composition on the influence of humidity on coating properties.

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# Simultaneous stress and weight measurements for particulate films made from capillary suspensions

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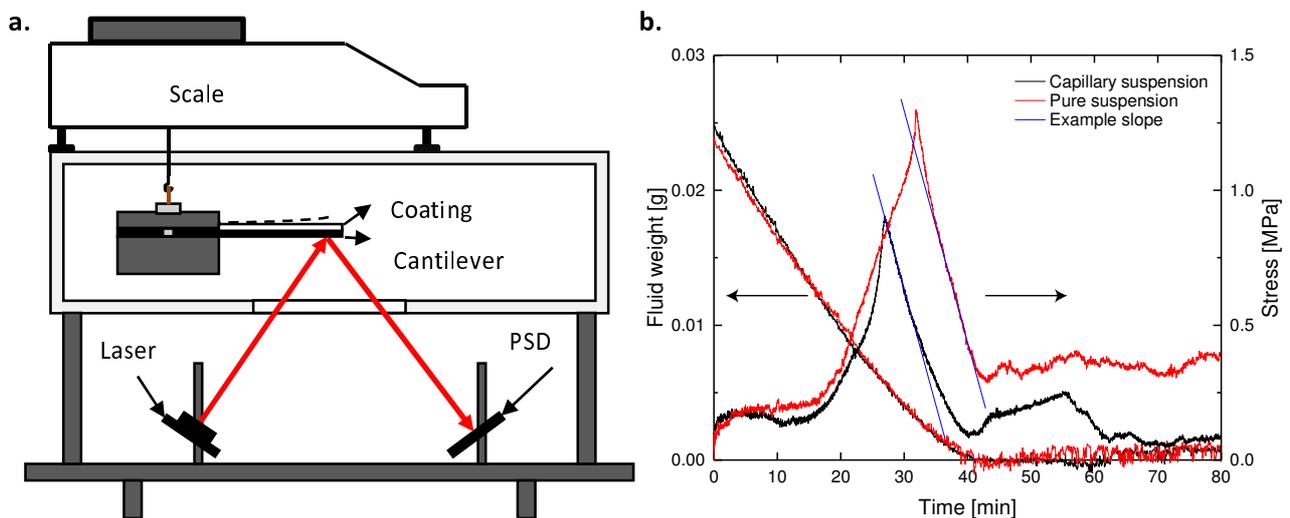
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Cracking and particle mobility are a significant problem in the drying of films from hard sphere suspensions. One pathway to avoid these problems is by using capillary suspensions [1]. In the pendular state, the preferentially wetting secondary fluid forms capillary bridges between the particles. The capillary forces from such bridges induce the formation of a sample-spanning particle network [2, 3], which limits the direction of particle motion during film drying and the capillary force of the bridges counters the capillary force within pores generated by evaporation. Crack-free films can be produced at thicknesses much greater than the critical cracking thickness for a suspension without capillary interactions, and even persists after sintering. This method is applicable to a broad range of materials and can be easily implemented using well-established industrial methods.

An in situ weight and stress measurement of a drying film allows direct relation of dynamic changes in stress with its corresponding drying rate. The overall stress of a film can be measured using the cantilever deflection method [4] as the film dries in a temperature and humidity controlled chamber as shown in Figure 1a. Capillary suspensions, with a higher shear modulus, can lower the overall stress in the film while drying, as shown in Figure 1b. Even though no visible cracks occur in either film, a characteristic increase and then relaxation occurs. Capillary suspensions change the shape of the stress profile as a function of drying time where similar slopes are present at different stages of the stress relaxation. Variation with drying temperature and humidity are also discussed.



**Figure 1** a. In situ stress and weight measurement apparatus with controlled drying chamber. b. Stress development and weight loss data of a pure suspension compared to a capillary suspension showing lower peak stress as well as a variation in peak shape.

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# 2D Hierarchical Organization of Semi-Fluorinated Alkanes in Nanometric Surface Domains and Giant Spherulites

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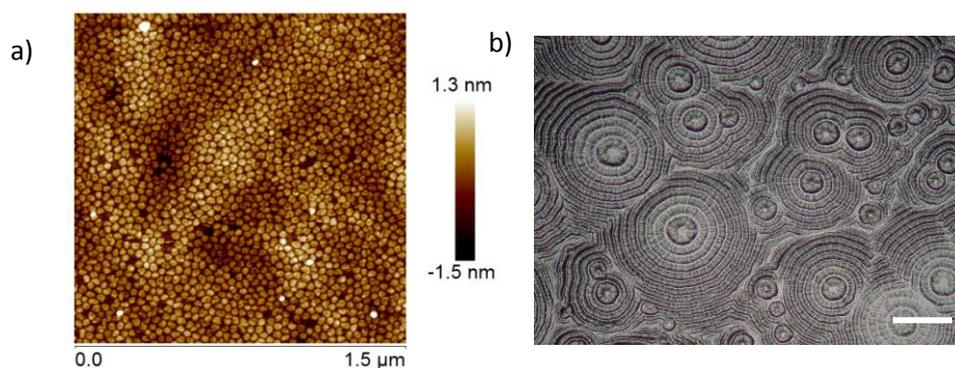
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When compressed as monolayers on water or deposited onto solid surfaces, semi-fluorinated alkanes  $C_nF_{2n+1}C_mF_{2m+1}$  (*F<sub>n</sub>H<sub>m</sub>* diblocks) form monodispersed circular nanodomains, one molecule in height and tens of nanometers in diameter [1] [2]. While there is some controversy about the existence of these domains in the dilute phase and also about the conformation of the *F<sub>n</sub>* and *H<sub>m</sub>* segments, we show by infrared reflection-absorption spectroscopy (IRRAS) and atomic force microscopy (AFM) measurements that the nanodomains do exist at large molecular areas (zero pressure, Fig. 1a) and remain unchanged when the film is compressed. Contrary to the usual assumption that the *H<sub>m</sub>* moieties would adopt a disordered liquid state, we show that the latter are in an ordered, crystalline-like state, like the *F<sub>n</sub>* moieties, and that they are tilted by  $\sim 30^\circ$  with respect to the normal to the monolayer [3]. Investigation of the rheological behavior of monolayers of *F<sub>n</sub>H<sub>m</sub>* diblocks by interfacial shear rheometry reveals that the surface domains form 2D gels even at zero pressure, which is quite unique compared to the gelation behaviors reported so far [4]. Surprisingly, we recently found that, when casted as thicker films ( $\sim 3\text{-}4\ \mu\text{m}$ ), *F<sub>n</sub>H<sub>m</sub>* diblocks form non-birefringent ring-banded spherulites (Fig. 1b) that display a succession of pronounced valleys and ridges ( $\sim 1.8 \pm 0.2\ \mu\text{m}$  in height) [5]. Finally, we also report the first case of dynamic conversion of radial to ring-banded spherulite morphologies.



**Figure 1** a) Height AFM image of a LB film of *F8H16* transferred on silicon wafers at  $0\ \text{mN m}^{-1}$  ( $53 < A < 60\ \text{\AA}^2$ ); b) optical micrograph of ring-banded *F10H16* spherulites; scale bar  $100\ \mu\text{m}$ .

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# Structure and Interactions of Lipopolysaccharide Layers

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Gram-negative bacteria, including key pathogenic species such as Escherichia and Salmonella, have a distinct protective outer membrane, mainly consisting of bacteria-specific lipopolysaccharides (LPS). Many antibacterial agents (ABAs) exploit electrostatic and hydrophobic interactions to disturb the membrane, aiming to weaken its protective and regulatory functions. To understand such interactions on a fundamental level, model bacteria membranes consisting of LPS or mixed phospholipid-LPS layers have been used to study their interactions with peptides. However, how the LPS architecture and solution conditions may affect the membrane structure and inter-membrane interactions has not been systematically studied.

Here, the adsorption of LPS (Ra mutants) on mica and the surface forces they mediate were studied using a surface force apparatus (SFA). The effects of temperature, divalent cations and the presence of a cationic antimicrobial peptide on adsorbed LPS surface layers were investigated. Our results show that LPS-Ra adsorbed weakly onto mica in water, and the SFA data indicates that the surface layers were squeezed out as the two surfaces approached each other. However, upon addition of calcium cations at near physiological concentration (2.5 mM) at room temperature, a LPS bilayer or multilayer on mica was observed, as indicated by a hard wall repulsion at surface separations of 20 to 40 nm. At temperatures (40 °C) above the LPS-Ra Krafft transition temperature (36 °C), LPS layers could be squeezed out at 200 and 400 mN m<sup>-1</sup> as indicated by 9 to 10 nm steps in the force-distance profiles and a reduced minimum hard wall separation of 9 to 10 nm, corresponding to the thickness of a single layer confined between the surfaces. Additionally, the frictional coefficient was significantly reduced from 0.2 to 0.05 at 40 °C. Furthermore, addition of cationic, surface-active oligoglycine to the adsorbed LPS layers led to bridging interactions, evident from an average adhesive force of 9 mN m<sup>-1</sup>, indicating the potential of the oligoglycine tetramer as a bacterial coagulant.

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## Getting the inside view of colloids with a SAXS/WAXS instrument

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Small Angle X-ray Scattering (SAXS) is proving to be a powerful technique for getting information related to the structure of nano-materials. By recording the x-ray scattering pattern, one obtains reciprocal space information that can be transformed or modeled to extract real-space information from the sample [1]. Information such as nanoparticle size, size-distribution and surface to volume ratio can be obtained in the range from 1 nm to beyond 100 nm. This is related to form factor of particles. Furthermore, particle interactions in colloids are readily obtained, as known as structure factor.

The method requires little sample preparation, is non-destructive and in contrast to microscopy probes a volume of the sample thus giving a statistically meaningful result. When combined with Wide Angle X-ray Scattering (WAXS) one can also get information on crystalline structure.

A broad range of materials and applications can be addressed by SAXS and WAXS techniques, ranging from soft condensed matter, polymers, bio-materials to nanoparticles, fibers and even structured surfaces which can be measured in the Grazing Incidence (GISAXS) geometry. This paper presents results from various material systems including biological solutions, nano-particles, highlighting how the provided information can be complementary to other analytical methods.

A short review of the considerable progress made in laboratory SAXS/WAXS instrumentation such as high brilliance microsource and advanced detectors will be done. Rapid measurements and high data quality opens the way towards dynamic measurements with parameters like temperature, humidity, flow, DSC as well as high precision structure resolutions on highly diluted and low contrast solutions, that is ideally suited for the study of most demanding colloidal systems.

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# Phase behaviour of Bowl-Shaped Colloids

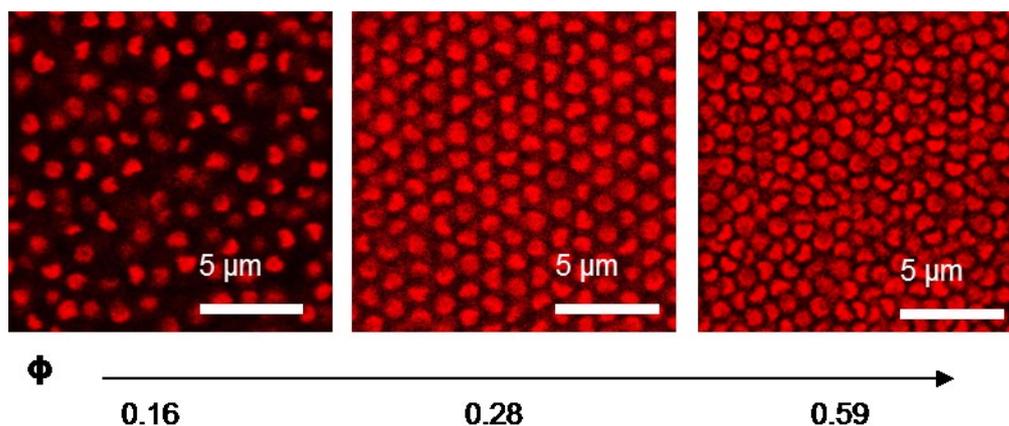
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By nanoengineering spherical composite microgels anisotropic bowl-shaped colloids can be obtained [1,2]. Here, we study the full phase behavior of bowl-shaped colloids consisting of a polystyrene core surrounded by a crosslinked poly(N-isopropylmethacrylamide) shell that possess soft repulsive interactions in deionized conditions. We find using confocal laser scanning microscopy (CLSM) that with increasing number density a transition from a fluid into a plastic crystal phase, with freely rotating particles, to a glassy state occurs (Fig. 1). Compared to their spherical counterpart, the glass state occurs at a significantly lower volume fraction for the bowls, indicating that the small shape change already frustrates crystallization. Moreover, quantitative analysis of the positional and orientational order shows that the plastic crystal phase possesses quasi-long range translational order and short-range orientational order, while in the glass phase has neither quasi-long-range translational order nor-quasi-long range orientational order. We furthermore explore the plastic to glass transition by measuring the translational and rotational dynamics characterized by their respective mean squared displacements and diffusion constants.



**Figure 1** Observed phases for bowl shaped colloids: from left to right, fluid, plastic cristal and glass.

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# A time-dependent pH scanning of the acid-induced unfolding of Human Serum Albumin

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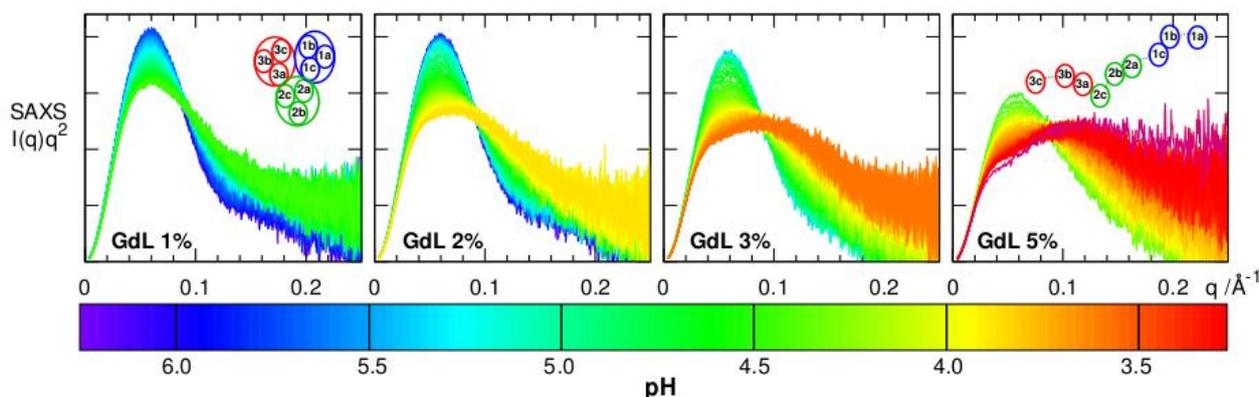
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The most abundant plasma protein, Human Serum Albumin (HSA), is known to undergo conformational transitions in acidic environment [1]. To avoid buffer effects and correlate global and local structural changes, we developed a continuous acidification method and simultaneously monitored the protein changes by both small-angle scattering (SAXS) and fluorescence [2], using a dedicated instrumental platform [3].

The progressive acidification, based on the hydrolysis of glucono- $\delta$ -lactone from pH 7 to pH 2.5, highlighted a multi-step unfolding involving the putative F form (pH 4) and an extended and flexible conformation (pH < 3.5). The scattering profile of the F form was extracted by component analysis and further 3D modeled, suggesting the rearrangement of the three albumin domains in a more elongated conformation, with a partial unfolding of one of the outer domains at this intermediate stage.

To test the stabilizing effect of fatty acids [4], here palmitic acid, we compared the acid unfolding process of albumin with and without ligand. We found that when binding the ligand the native conformation was favored up to lower pH values.

Our approach solved the problem of realizing a continuous, homogeneous and tunable acidification with simultaneous characterization applicable to study processes triggered by a pH decrease.



**Figure 1** SAXS data in the form of Kratky plot show the unfolding process of HSA as a function of the progressive acidification due to the hydrolysis of different amounts of glucono- $\delta$ -lactone (GdL).

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# Pattern deposition and surface forces

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The evaporation of a suspension of colloidal particles may leave behind deposits of well-ordered patterns. This is generally known as pattern deposition or the coffee ring effect. Several experimental studies show evidence of a direct relation between the electrical double layer mechanism and the deposits. Specifically, the deposits were found at different geometries for different values of the zeta potential of the particles or of the solid substrate on which the deposition occurs. Variations in the concentration of the electrolyte in the suspension further alter the geometry of the deposits. In this talk we will discuss the mechanisms by which surface forces such as the electrical double layer mechanism may influence pattern deposition.

We consider the spatiotemporal variations in the population of colloidal particles suspended in a volatile drop, while accounting for the coagulation of the particles and their adhesion to the solid substrate. We solve a dynamic advection-diffusion equation to monitor the transport of particle mass in the volatile liquid. The rate of adhesion of particles to the solid substrate is modelled using the interaction–force boundary layer theory. The coagulation of particles in the solution is modelled using the augmented Smoluchowski theory. Both theories account for the presence of surface forces in terms of energy barriers to particle-particle or particle-solid attachment. We find that fast adhesion of particles to the solid substrate and fast diffusion of the particles in the liquid disperse the spatial distribution of the deposits. However, fast coagulation of particles and fast evaporation of the liquid support the deposition of well-defined patterns of particles.

# Microfluidic-assisted determination of phase diagrams of aqueous two-phase systems within double emulsion drops

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Aqueous two-phase systems (ATPSs) form by the separation into two distinct thermodynamic phases of at least two sufficiently dissimilar molecules dissolved in water at high enough concentration. These systems find multiple applications, including the separation and purification of biomolecules, organelles or cells, the performance of bioconversions with improved reaction yields, or the fabrication of microcapsules [1]. However, all of these applications depend critically on the compositions of the two phases. It is therefore essential to characterize the phase diagram of the particular mixture to be used for a certain application. Here, we report a versatile approach for the rapid determination of phase diagrams of ATPSs. This approach involves encapsulation of two dissimilar molecules within the aqueous cores of water-in-oil-in-water double emulsion drops, fabricated using glass capillary microfluidic devices [2]. Initially, the concentration of molecules within the drop cores is low enough to ensure a uniform encapsulation in the one-phase region of the phase diagram. Later, double emulsions are subjected to osmotic pressure to increase the concentration of molecules in their cores and ultimately cause their phase separation. Measurements of the osmotic pressure and acquisition of bright field and confocal fluorescence images of the resultant phase-separated drops enable determination of the tie-lines and binodal curve of the phase diagram. Because this strategy encapsulates molecules in the small volume of an emulsion droplet, and because double emulsion drops encapsulating different compositions can be forced to align into a single tie-line upon collection in a medium of fixed osmolarity, the kinetics of the phase separation is accelerated and the number of samples to be prepared for tie-line determination is reduced. Therefore, our strategy enables determination of phase diagrams of ATPSs in just a few hours, in stark contrast to conventional phase diagram determination that requires from several days to several weeks.

**Acknowledgements** LRA acknowledges funding from Juan de la Cierva-Incorporacion program (IJIC-2014).

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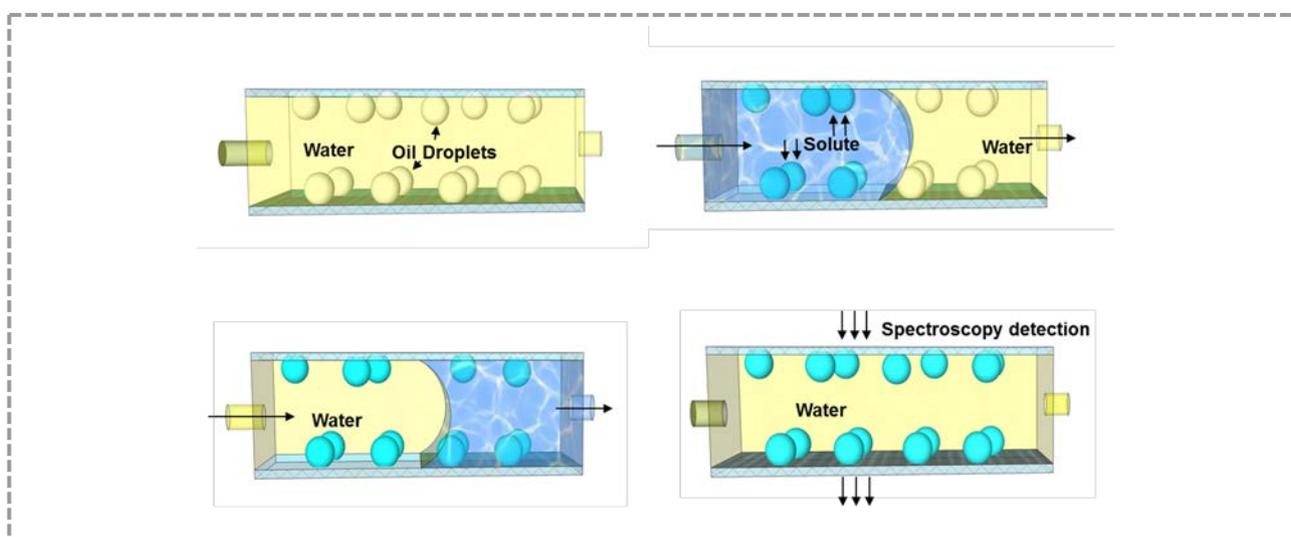
# Surface Nanodroplets Enabled Micro-Sampling Platform for Concentrating and Analysing Trace Hydrophobic Solute in Water

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Preconcentrating a hydrophobic analyte from its aqueous solution into a dispersive oil phase is a common approach to achieve high sensitivity in quantitative analysis. Dispersive liquid-liquid microextraction (DLLME) has drawn great reach interest in last decade as a highly effective approach for preconcentrating and separation. However, the completed process and multiple steps required by this method significantly reduce its efficiency for this approach. In this work, we propose a novel approach of surface nanodroplet-enabled concentrating and quantitative analysis of trace of hydrophobic solutes in aqueous solutions. This approach offers unprecedented advantages in the following aspects: The solute is enriched into oil-like nanodroplets on the substrate directly from water without presence of any dispersive organic solvent. Therefore, the concentrating factor of the hydrophobic solute in the droplets is higher, compared to the widely-used dispersive liquid-liquid microextraction. Moreover, the concentrating and analysis of the hydrophobic analyse is achieved in one step, which avoids the most time-consuming step of separation of the concentrated solute from dispersions before analysis, and hence allows for analysis of the extractant varying with reaction time. Finally, the long lifetime and temporal stability of surface nanodroplets allow for long-term concentrating and analysis process. Several applications are demonstrated in this work to prove the surface nanodroplet-enabled concentrating and analysis is general and applicable to a wide range of hydrophobic compounds in water.



**Figure 1** Sketch shows a typical procedure of extraction, separation and quantification of analytes by surface nanodroplets.

**Acknowledgements** The Authors acknowledgesThe financial support of Australian Research Council (FT120100473) and RMIT Vice-Chancellor’s Postdoctoral Fellowship.

# Pattern Deposition of Colloidal Particles into a microfluidic chamber: Role of DLVO Forces and Mechanism Proposition

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Colloids play a fundamental role in a huge number of technological and biological domains, such as water treatment, industry, printing, drug delivery and many others. Controlled colloids deposition -pattern deposition- over surfaces is crucial for both exploiting collective properties of particles and their integration into applicative devices. Recently, many companies have shown an increase interest in deposition patterns from an evaporating suspensions or solutions as an efficient way to avoid expensive fabrication procedures like photolithography. However, the deposit shape obtained from an evaporating thin film of liquid containing colloidal particles still challenging tremendous academic researches. Various patterns such as ring-like structure, central pump, and uniform deposit can generated during the evaporation of sessile droplet depending on many interplaying forces, transport phenomena, and evaporation dynamics governing the ordering. Nevertheless, freely evaporating droplets (unconfined geometry) mostly lead to unprecedented regularity and unreproducible patterns.

In contrast, evaporation of suspension from confined geometry (e.g., two parallel plates, "curve-on-flat" and other geometries) imparts exquisite control over the drying dynamics and associated flows, which in turn, allows for crafting complex deposit patterns with high regularity, well defined and controlled repetitive manner. In order to be able to control the deposited patterns and functionalize them, one should have a thorough insight into the mechanism and stages of the ordering process, which is weakly established yet.

In this work, we apply a simple model system comprised from two parallel plates with rectangular geometry. The system studied involves aqueous suspension of varied size latex particles evaporating from a micrometric gap on SiO<sub>x</sub> substrate. During the evaporation, the aligned contact line moves in a "stick-slip" motion, where the deposition occurs in the stick mode producing periodic parallel stripes. Tuning different factors such as particles size, concentration, presence of electrolytes and their concentrations, water evaporation rate, and presence of surfactants has shown direct impact on the obtained pattern inside the chamber, and enable us to predict the length scales of periodicity, height, and width of the stripes pattern when obtained, as a function of the influencing variables on the evaporative self-assembly process.

Finally, we use our findings in order to identify and quantify the influence of the different physical mechanisms taking place during the experimental procedure while shedding the light on the colloidal forces involved in, besides to the role of Derjaguin-Landau-Verwey-Overbeek (DLVO) forces.

# Soft electrodes for blue energy production and water desalination

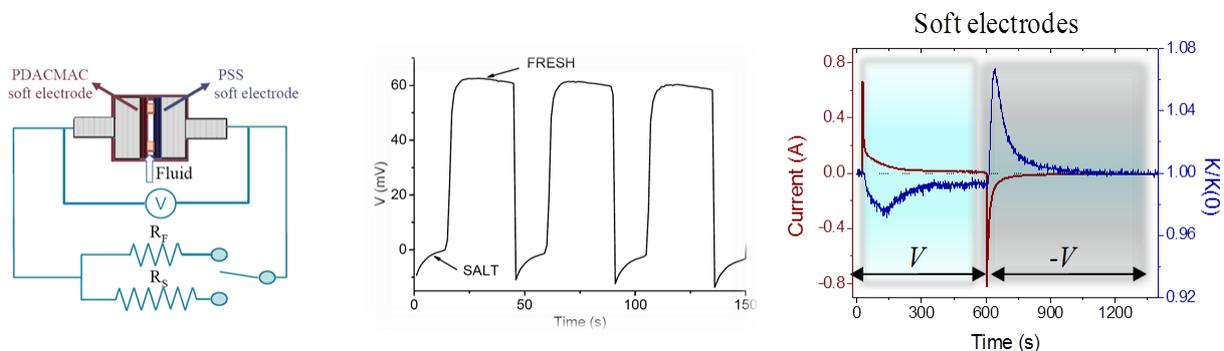
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There is a growing interest in the use of electrodes with high capacitance for both energy harvesting from salinity gradients and, vice versa, for desalinating aqueous solutions [1,2]. One way to do this is by taking advantage of the huge capacitance associated to the Electrical Double Layer formed when these interfaces are in contact with ionic solutions. This allows the adsorption of ions (Capacitive Deionization, CDI) or, the reciprocal process, the generation of energy by exchanging solutions with different salinities (Capacitive Donnan Potential, CDP, and Capacitive Double Layer Expansion, CDLE).

In CDI as well CDP, the use of ionic exchange membranes adjacent to electrodes plays a very important role. An alternative which has proved very efficient [2] is the coating of the electrodes with layers of adsorbed polyelectrolyte, respectively, cationic (PDADMAC) and anionic (PSS). The Donnan potentials of the layers establish a potential difference between the electrodes which changes with the salinity of the solution in contact. Additionally, the layers can control the adsorption and release of ions, and improve the efficiency in the case of desalination. In this contribution, we describe theoretically the processes taking place in the electrodes in both kinds of processes, and show experimental results concerning the power available and the amount of salt which can be extracted from solutions using such electrodes (examples are provided in Figure 1). The name proposed for them, “soft electrodes”, reminds of the denomination given to particles consisting of a rigid core and a polyelectrolyte shell, widely investigated because of their particular physical properties and potential applications.



**Figure 1** Left: schematics of the experimental cell used for energy extraction and desalination with soft electrodes. Center: typical time evolution of the open-circuit potential when fresh and salt waters are exchanged. Right: current and conductivity variations during desalination.

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**Acknowledgements** The financial support of MINECO, Spain (Project FIS2013-47666-C3-1-R), and Junta de Andalucía, Spain (Project PE2012-FQM694) is gratefully acknowledged.

# Effect of surfactant dynamics on microfluidic emulsification

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The microfluidic emulsification is a rapidly growing scientific area providing an advantage of formation of uniform drops of micrometer size and manipulating them in controlled way. Surfactants are broadly used in emulsification processes to stabilize drops. In microfluidic, where drops are formed on the time scale of milliseconds, dynamic effects related to surfactant transfer and adsorption become extremely important. In this study, using high resolution high-speed video-recording, we explore in a flow-focusing microfluidic device the effects of surfactants on the dynamic regimes of aqueous drop formation in an organic phase, the size of formed drops and their coalescence in the microchannel.

It is shown that dynamic interfacial tension is a key parameter for controlled drop production. Under the same flow rates of continuous and dispersed phases, addition of surfactant often changes the flow regime from dripping to jetting, what results in a wider drop size distribution. Using data on dynamic surface tension of the surfactant of interest, the range of flow rates for production of uniform surfactant-laden drops in the dripping regime can be estimated from the flow map of surfactant-free system.

The size of formed drops increases with the increase of ratio of flow rates of dispersed to continuous phase,  $f$ . For the drops with size smaller than the channel width the growth is slow, proportional to  $f^{0.1}$ , whereas for plugs with size larger than the channel width the size is proportional to  $f$ . The power law exponent is practically independent of surfactant type.

It is found that the presence of ionic surfactant can facilitate drop coalescence in the channel, if the drop size is larger than the channel depth. This effect can be a result of surfactant redistribution under the high shear stress near the channel wall.

The effect of surfactant on the flow patterns is also studied using a two-colour PIV technique. The technique measures velocity profiles in both continuous and dispersed phases simultaneously, thus revealing the effects that the presence of surfactants has on the local flow fields.

**Acknowledgements** The financial support of Engineering and Physical Sciences Research Council (EPSRC), UK, through the Programme Grant “MEMPHIS – Multiscale Examination of Multiphase Physics in Flows” (EP/K003976/1) is acknowledged.

# Radioactive soil decontamination: investigation of fine colloidal aggregates extraction from soil via froth flotation technology

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After a nuclear accident such as Fukushima Dai-ichi nuclear power plant accident in Japan in 2011, radioactive cesium aerosols are released and transported by wind and rain water to the neighboring soils surface [1]. Cesium solubilized in water can penetrate into soil to contaminate it by fixing on the hydrophilic clay particles by strong ionic interactions. These minerals, and especially the varieties called illite and vermiculite, contain adsorption sites located on layer edges on which cesium ions can selectively sorb in presence of other competing ions like sodium or calcium. Furthermore, adsorption is known to be nearly irreversible and very resistant to washing [2].

Despite the numerous soil decontamination technologies such as soil washing, magnetic separation, electrokinetic processing, phytoremediation methods [3,4], there is a need for environmentally eco-friendly process that will limit the production of secondary wastes and allow the handle of the high volumes of contaminated soil. In this context, CEA (French Atomic Energy Commission) propose a froth flotation process as innovative and cost-effective alternative technology to decontaminate radio-contaminated soil by selectively extracting the fine clay particles containing the majority of contamination in a minimized volume or mass (15-30% of initial weight).

In the present study, supported by the French Agence Nationale de la Recherche (ANR) through DEMETERRES project in collaboration with AREVA and VEOLIA, the flotation technology is used in continuous mode to extract, with air bubbles, fine clay particles from various soils. To capture clay particles by attachment to dispersed bubbles into a soil slurry contained in a 8 cm diameter column (160 cm height), a cationic surfactant (TTAB) is used to adsorb on the negatively charged clay particles surface. The surfactant modifies the hydrophobicity to different extents depending on initial concentration in the slurry. After the adaptation of this process to soil flotation, several soils, presenting various textural characteristics, were floated and compared. The effects of processing parameters, including TTAB/soil ratio, froth residence time, suspension concentration and air flow rate, upon fine particles extraction performance to determine the most significant variable that affect flotation and obtain the operating conditions which led to the best performance. TTAB/soil ratio, froth residence time ranges, suspension concentration ranges and air flow rate will be given and discussed. Finally, the selectivity of the process on the fine particles was investigated and will be discussed. Moreover, scale-up studies were performed at pilot scale on a 20 cm diameter column, 2 m height. Flotation results showed that fine particles extraction from soil is feasible thanks to attachment to air bubbles and exhibits excellent floatability and selectivity. The results obtained at lab and pilot scales evidenced good agreement which provides valuable evidence to support the technical viability of the soil flotation process for future exploitation at industrial scale. This study provides a new direction to extract fine particles from complex soil system by flotation technology.

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# Pheophorbide a in action. A simple membrane model to understand its release from polymer nanocarriers.

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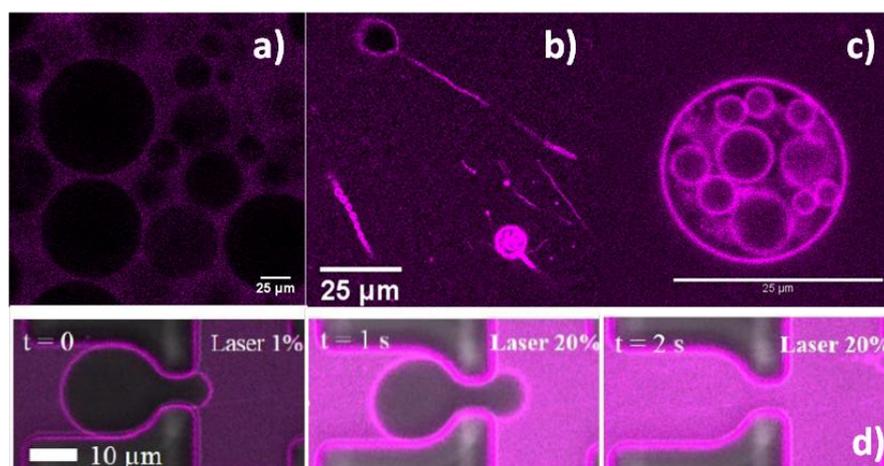
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Polymer-based nanocarriers have great potential in nanomedicine to incorporate and transport active drugs. Nevertheless, after decades of work on drug delivery and cancer treatment, clinical translation remains limited, due to numerous biological barriers and challenges. The use of simple model membranes is a valid tool to help interpreting the *in vitro* results, often complicated by the intrinsic variability of cell culture. It is essential to separate the physicochemical aspects from the biological ones.

In this context, our approach on photodynamic therapy (PDT) assessing the delivery of photosensitizers from polymeric carriers [1, 2] appears as a powerful one, since photosensitizers have a dual role, being a probe for imaging and the specie producing the drug (reactive oxygen species formed from the interaction of the excited photosensitizer with oxygen). As for oncology, the mechanisms of the release from nanocarriers and their internalization inside cells are not well elucidated yet [3]. We therefore begun an ambitious study on the effect of photosensitizers encapsulated in polymer nanocarriers on giant unilamellar vesicles (GUV). Confocal microscopy on GUV gives us experimental evidence of important modifications in lipid membranes put in contact with solutions of loaded polymer nanocarriers (Fig 1a-c). Dialysis and fluorescence experiments inform us on the efficiency of pheophorbide a release from polymer carriers. The results can be related to therapy efficiency [2]. Besides, by using a microfluidic approach, we study in real time, by confocal microscopy under flow, the interaction of GUV with polymer carriers bearing pheophorbide a. Increasing light excitation promotes the deformation of the GUVs and their release from the traps (Fig 1d).

All our results help to rationalize the influence of the nature and composition of the carriers on their release abilities.



**Figure 1** Confocal microscopy images of GUVs after interaction with a solution containing pheophorbide encapsulated in polymeric self-assemblies. a) PEO-PS ; b)-c) PEO-PCL; d) Effect of illumination on a trapped GUV.

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# Delivery Systems for Low Molecular Weight Payloads: Composite Coacervate/Polyurea Core-Shell Capsules

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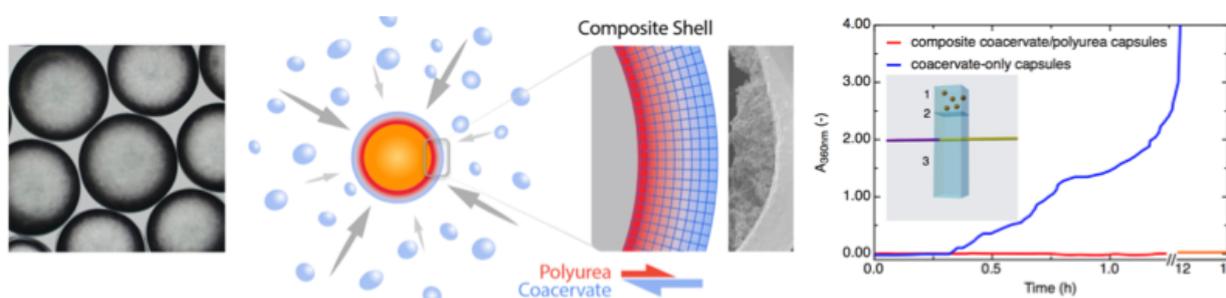
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The controlled delivery of active ingredients in complex media is required in an increasing number of applications, including home and personal care products, foods, agriculture, or pharmaceuticals[1–6]. However, encapsulation remains very challenging for small molecules to be stabilized in harsh environments, in particular for aldehydes, ketones, and other phytochemicals, e.g those used as fragrances or flavors [1,2]. For example, concentrated surfactant solutions, as used in many personal care products, exert a strong osmotic pressure and cause diffusive losses of the encapsulated compounds.

Here, we synthesize core/shell capsules with composite shells, combining a strong chemical barrier formed by synthetic polyurea with the outstanding adhesive properties of protein-based complex coacervates. We form coacervates [3] from a protein and a weak polyanion, followed by interfacial deposition of this separated coacervate phase on the oil drops, thereby creating a coacervate shell. A polyurea membrane is then synthesized *in-situ* from the interface between the coacervate and the oil core, resulting in a composite polyurea/coacervate shell.

We characterize these capsules by microstructural and compositional analysis of the shell material, nanoindentation/micromechanics, and *in-situ* stability testing in model applications, tracking both the capsule morphology and the release of the encapsulated payloads. Complementary human sensory tests support the physicochemical data and confirm the enhanced barrier properties of composite coacervate/polyurea vs. classical coacervate capsules.

The core/shell capsules described here combine the adhesive properties of coacervates, as found in ‘biological glue’-type materials [1,3], with the low permeability of traditional, purely synthetic polyurea microcapsules. Moreover, the approach used here can easily be implemented in a simple one-pot experimental setup since the core/shell structures developed here form spontaneously upon mixing due to the favorable three-phase interfacial thermodynamics of the oil/coacervate/water system.



**Figure 1** – From left to right: Sample micrograph of composite coacervate/polyurea core/shell capsules (capsule mean diameter: 150  $\mu\text{m}$ ); schematic of the combined coacervation/interfacial polymerization process: coacervate droplets (blue, size range:  $\mu\text{m}$  to tens of  $\mu\text{m}$ ) spontaneously deposit at the oil core drops (orange); close-up schematic and SEM micrograph of the composite membrane; comparison of the stability of composite vs. classical capsules, measured in a concentrated surfactant solution via the absorbance caused by molecular losses through the shell.

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# P-SULFOCALIX[6]ARENE AS NANOCARRIER FOR CONTROLLED DELIVERY OF DOXORUBICIN

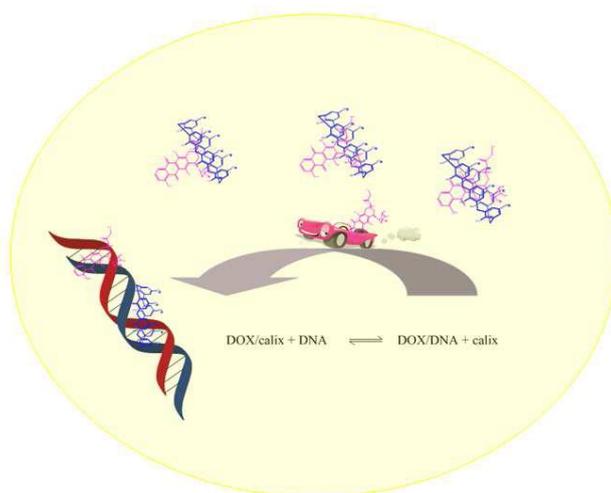
Francisco José Ostos<sup>1\*</sup>, José Antonio Lebrón<sup>1</sup>, Pilar López-Cornejo<sup>1</sup>, María Luisa Moyá<sup>1</sup> and Manuel López-López<sup>2</sup>

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Given the high toxicity of the anthracycline antibiotic called doxorubicin (DOX), it is relevant to look for nanocarriers that, decreasing the side effects of the drug, were able to transport it towards a therapeutic target. Accordingly, the encapsulation of DOX by p-sulfocalix[6]arene (calix) has been studied (Figure). The interaction of DOX with the macrocycle, as well as with DNA, has been investigated and the equilibrium constant for each binding process estimated. Results showed that the binding constant of DOX to DNA, KDNA, is three orders of magnitude higher than that to calix, Kcalix. A multidisciplinary study has been done to demonstrate the ability of calixarenes to encapsulate DOX molecules, as well as the power of the DOX molecules included into the inner cavity of the macrocycle to bind with the DNA. Cytotoxicity measurements were done in different cancer cell lines to probe the decrease in the toxicity of the encapsulated DOX, demonstrating thus the decrease of its side effects in the human organism. The low toxicity of calixarenes has also been demonstrated for different cancer cell lines.



**Figure.** Encapsulation of free doxorubicin molecules in solution diminishing their side effects.

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## Tactile and hair–hair friction behavior of hair fibers

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There is an increasing interest in finding analytical techniques that could be used to predict various sensory characteristics. Many of the sensorial aspects associated with hair are related to friction. Friction between hair fibers is related to their manageability and volume and friction between a human finger and hair more related to the sensorial touch. The nanotribology of hair was evaluated using the AFM fiber probe technique to measure the friction between two single hair fibers. Tactile friction was measured using a ForceBoard™, on the root, middle and tip part of the hair, both along and against the cuticles. A clear directional effect was observed with higher friction against the cuticles. Hairs treated with a proprietary repairing agent containing ceramides, show a slight trend towards a lower tactile friction coefficient along the cuticles but more evident against the cuticles, compared with the untreated reference and also less difference between the two stroking directions. This indicates that most likely part active is also present at the surface of the hair, where the lower friction against the cuticles may be due to a smoothening of the fiber which could act to reduce the interlocking effect. The AFM fiber-fiber friction results show a higher friction coefficient between treated hair fibers, indicating that the nature of the hair surface is changed upon treatment. In damaged hair, naturally occurring ceramides and fatty acids are missing, resulting in coarse, dry and dull hair. Understanding the bio-tribological effect of ceramides help to optimize the protection and restoration of hair fibers and consequently improve the surface and appearance of the hair. The unique combination of techniques and protocols developed in this work to evaluate the tribological effects of hair treatments is promising. In future studies it would be highly interesting to link the frictional response with quantified sensorial attributes.

# Analysis of Drug Delivery Systems with SAXS in the Laboratory

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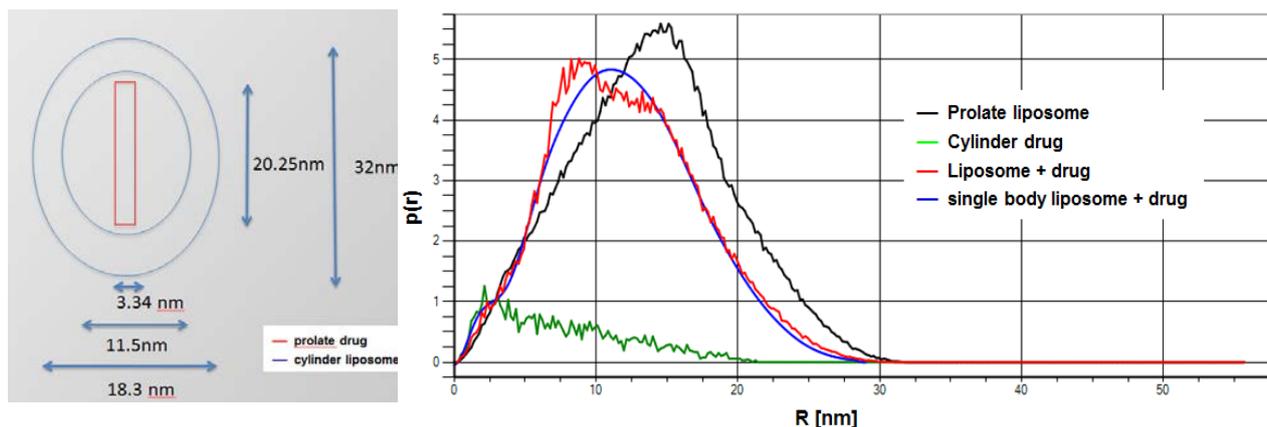
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Small-Angle X-ray Scattering (SAXS) draws increasing attention in the field of pharmaceutical engineering. SAXS is a versatile technique used for shape and size characterization of nanostructured materials between 1 nm and 200 nm. Biological samples, like proteins or viruses are already well known to be investigated with SAXS. Furthermore drug delivery systems like drug loaded vesicles (see example in figure 1), where size and shape parameters of the vesicle and the drug are found or granulate powders, where the internal surface obtained by SAXS correlates with the tablet hardness, are interesting examples of applications in pharmaceutical research.

In this contribution we present selected applications of biological samples, employing a multifunctional laboratory Small and Wide Angle X-ray Scattering (SWAXS) system, the SAXSpoint. The SAXSpoint system enables SAXS and WAXS studies at ambient and non-ambient conditions, GI-SAXS, in-situ tensile SWAXS. The system provides simple operation, short measurement times and excellent angular resolution, enabled by a smart beam formation concept which includes a brilliant X-ray source, advanced X-ray optics and optimized scatterless collimation while maintaining a laboratory-friendly compact size and small footprint.

Different scattering studies on biological and pharmaceutically relevant samples were performed on the presented SAXSpoint system. Some of the samples required high resolution, i.e. a very low minimum scattering angle in order to resolve large structural dimensions. The unique sample-positioning mechanism enabled WAXS measurements to determine crystallinity without re-aligning any part of the SWAXS system. The presented studies clearly show that high-resolution and high-quality SWAXS data can be obtained with a laboratory SWAXS system.



**Figure 1** Study of a liposome drug carrier system. Data, obtained from a SAXS-measurement, yielded with aid of single body simulation (simulated Pair Distance Distribution Function on the right side) in the depicted model of the drug-loaded liposome (on the left side).

# Wetting on Magnetically Actuated Superhydrophobic Surfaces

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Superhydrophobicity is defined by very low surface wettability. Combining hydrophobic surface chemistry and (multiscale) roughness give rise to low contact angle hysteresis ( $<10^\circ$ ), high contact angle ( $>150^\circ$ ) and low sliding angle. Droplets of water on such surfaces can reside in the Cassie-Baxter state. Also called fakir state, the droplet sits on top of the textured surface with trapped air underneath [1], inducing very easy sliding out of the surface if slightly inclined [2]. Nevertheless, this state of wetting can transit to another (irreversible) state where the drop is anchored in the roughness: the Wenzel state [3]. In this case, the droplet is preventing from sliding [4].

Presently, the production of superhydrophobic surfaces is well documented, but the characteristics (geometry, roughness) of such surfaces are fixed once and for all during their synthesis, unlike some natural surfaces which can rejuvenate their roughness [5].

This work focuses on the development of superhydrophobic surfaces whose wettability can be controlled by an external magnetic stimulus. Formulating a network of elastomeric magnetic pillars allows the orientation of the pillars through magnetic forces, hence an adaptable surface roughness. The wetting properties of these surfaces can then be followed, both in a Cassie-Baxter (fakir state) or in a Wenzel state (impaled state). The preparation and the characterization of these surfaces will be first presented, and then the control of the displacement and the sliding of a water droplet using magnetic actuation will be exposed.

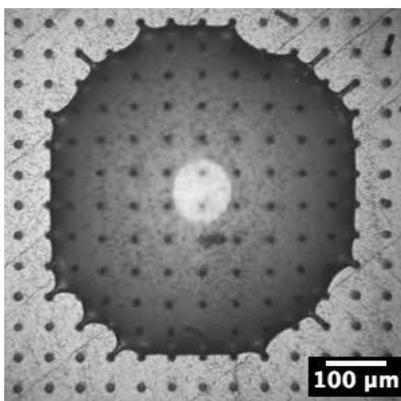


Figure 1 : Dewetting of pillars in Wenzel state

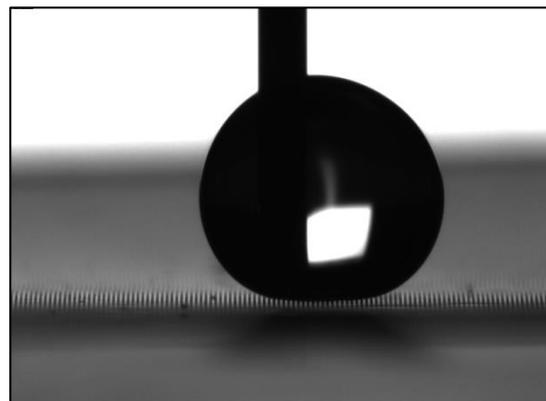


Figure 2 : Swelling of droplet in Cassie state

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# Low-Voltage Electrowetting on Multilayer-Dielectrics

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Electrowetting on dielectric (EWOD) is the wettability increase of a conductive droplet on a dielectric layer through applying voltages. This principle is used to realize deformation, fusion as well as division of droplets for various practical applications, such as displays, liquid lenses and lab-on-a-chip systems [1, 2]. One of the biggest obstacles to improve electrowetting is its high voltage demand (25-50 V). This results in complicated electronics, difficulties in on-line investigation with electrical methods, high costs and raises problems, such as Ohmic warming and electrolysis of droplet liquid.

This contribution presents the development of a low-voltage EWOD electrode and the characterization of its electrowetting performance at low alternating voltages with electrochemical impedance spectroscopy (EIS).

The EWOD electrode was constructed as a multilayer stack. It is based on an electrode substrate with dielectric tantalum oxide and hydrophobic silane. A homogenous thin layer of tantalum oxide was generated through anodization. Its thickness and capacitance were investigated with ellipsometry and EIS. Its relative permittivity and layer growth coefficient were determined to be 26.7 and 2 nm/V respectively. Both values are comparable to the literature. A hydrophobic silane monolayer was realized through self-assembly. The surface hydrophobicity and roughness were analyzed through measurements of contact angle and contact angle hysteresis.

The low-AC-voltage electrowetting was on-line studied with EIS and optical imaging. An equivalent circuit model was developed to describe the droplet, the dielectric layers and the interfacial region in between. Influences of different parameters on the electrowetting were investigated. The experimental results showed good agreement with the theory for electrowetting at alternating voltages.

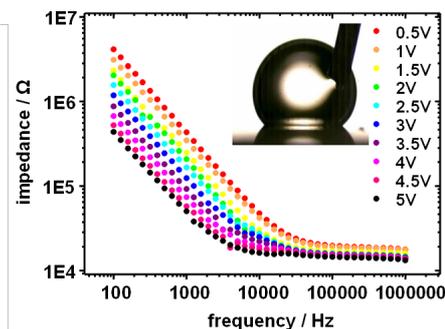


Fig. 1: Impedance spectra during electrowetting of a 3  $\mu$ L droplet at different low AC voltages.

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# The Reverse Coffee-Ring Effect: Wetting of *n*-alkane Molecular Films

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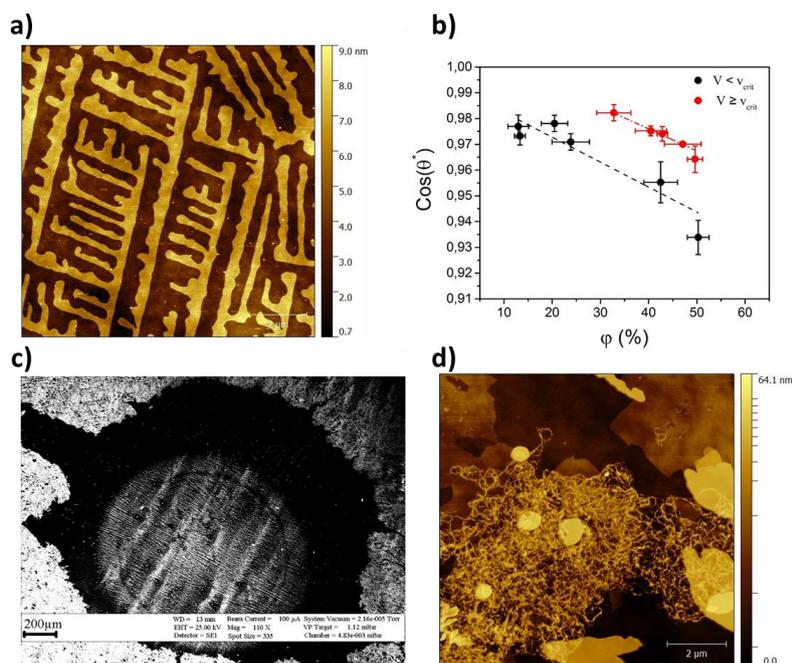
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We present a study of the wetting properties of silicon samples coated with a single layer of *n*-alkane molecules that self-assemble perpendicular to the surface. Previously, we have shown that the filling fraction of molecules ( $\varphi$ ) on the surface can be controlled by the withdrawal velocity ( $v$ ) of the silicon wafer from the preparation solution. [1] The initial filling fraction of molecules can be varied between  $\varphi = 10\%$  to  $\varphi = 50\%$  (Fig. 1a). After sample preparation, we measure the contact angle of a sessile drop of water placed over the patterned surface. The cosine of the apparent contact angle versus  $\varphi$  can be grouped in two regimes that depend linearly on  $\varphi$  (Fig. 1b). This is consistent with the Cassie equation for a chemically heterogeneous surface. We suspect that the separation in two regimes is due to the morphological differences that emerge from preparation conditions, e.g. patterned stripes ( $v \geq v_{crit}$ ) or dendrites ( $v < v_{crit}$ ), where  $v_{crit} = 0.8 \text{ mm/s}$ . After drop evaporation, the molecules migrate to the center of the area where the sessile drop was placed, much like a reverse coffee-ring effect (Figure 1c). Upon further examination we find that the original patterns restructure forming complex tail-like morphologies after drop evaporation (Fig. 1d). [2–4]



**Figure 1** a) AFM image of a silicon substrate patterned with a perpendicular layer of *n*-alkane molecules 4 nm high. This image is taken before placing a sessile drop of water. b) Contact angle versus filling fraction ( $\varphi$ ). c) SEM image of the region where the drop is placed after evaporation. d) AFM image after evaporation of the region where the drop is placed.

**Acknowledgements** T.P.C acknowledges the financial support of Fondecyt Iniciación 11160664. U.G.V acknowledges the financial support of Fondecyt Regular 1141105.

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# Viscous Drop Impact on Soft Deformable Substrates

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Drop impact phenomena have been studied extensively since the work of Worthington in the 19<sup>th</sup> century [1]. The reason for this interest is the importance of drop impact phenomena and their relevance in the industrial sector. Basic hydrodynamics of impact of Newtonian, non-Newtonian or multicomponent fluids on solid and liquid surfaces has already been investigated in details [2, 3]; however, drop impact onto soft deformable substrates remain less studied, despite the importance of this phenomenon for different fields, like, for example, agriculture, microfluidics or additive manufacturing.

The present experimental study focuses on the impact of a viscous drop onto soft surfaces of various elasticity. The experimental setup consists of a drop generator, the target substrate and the high-speed video system. Polydimethylsiloxane (PDMS) is used to coat the substrate. The PDMS films have been prepared by mixing the prepolymer with a cross-linking agent. The mixing ratio of the base solution and cross-linker imparts different cross-link density into the substrates which manifests itself in dynamic mechanical properties (storage and loss moduli). To examine the influence of the drop viscosity on the impact outcome, different concentrations of glycerine solution in water were used in the experiments.

Figure 1 shows water drop impacting substrates of three different mixing ratios. The initial spreading phase of the wetting is almost not affected by the softness of the substrate. However, the receding velocity is slowed down considerably by the softness of the impacting film. The drop contact radius at the end of the receding phase increases with the softness of the substrate. It is interesting that in some cases the substrate softness suppresses the drop bouncing.

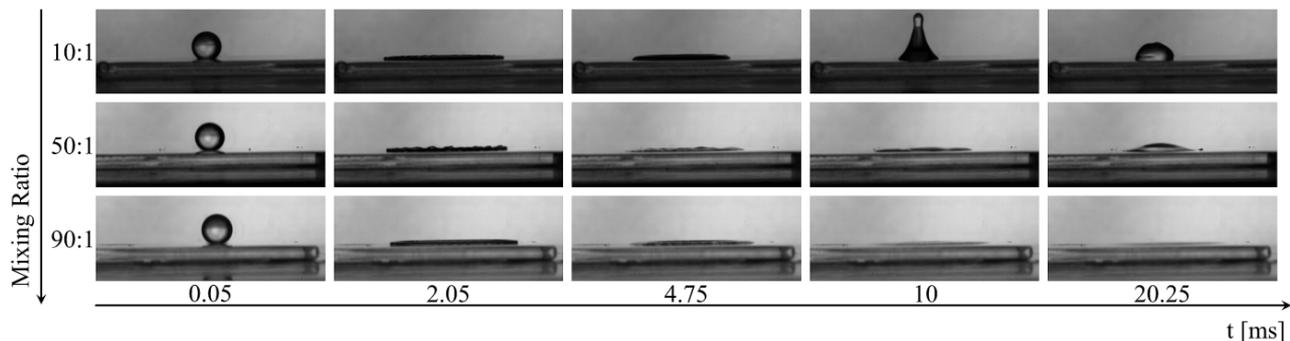


Figure 1: Water drop impacting different substrates from hardest (10:1) to softest film (90:1). The advancing stage is inertia dominated while the receding phase is influenced by the softness and wettability of the underlying PDMS films.

**Acknowledgements** This research was supported by the German Scientific Foundation (Deutsche Forschungsgemeinschaft) in the framework of the SFB-TRR 150 Collaborative Research Center, subproject A02 and Marie Curie Initial Training Network "Complex Wetting Phenomena" (CoWet), Grant Agreement no. 607861.

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# Gaseous nanobubbles as important components of solid/liquid interface.

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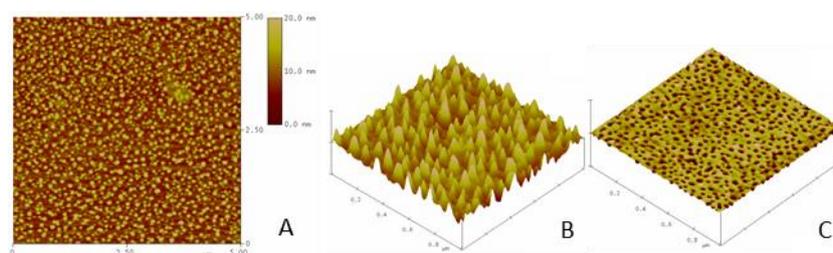
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Gaseous nanodomains in form of nanobubbles (NB) occupying hydrophobic surfaces immersed into aqueous solution attract steadily increasing attention. The existence of NBs as stable entity has been debated for a long time due to some thermodynamic contradictions. From Young Laplace equation and the dimensions of NB (radius  $\sim 10$ - $100$  nm;  $\sim 10$  nm height) follows that pressure inside NBs must be very high and therefore bubbles would dissolve in a sub-second time. However, the tapping mode AFM experiments performed in situ (Fig. 1A) have shown that NBs exist at the solid-liquid interface for several hours or even days.

Gaseous ambient (air) NBs on water-immersed polystyrene (PS) film affect its surface nanomorphology. Mild ( $\Delta p \approx -10$  kPa) short ( $\sim 5$  sec) pressure drop applied on aqueous phase triggers formation of NB imprints ranging from nanoprotusions (Fig.1B) to nanopinholes (Fig. 1C) depending on experimental conditions [1], [2]. This nanobubble-assisted nanopatterning proceeds in a single step under biocompatible conditions in deionized water at room temperature ( $20$  °C) in absence of any high-energy-demanding processes. Its mechanism is based on interfacial force and surface stress developed in PS film at nanobubble contact upon expansion. Nanobubble-assisted nanopatterning may have prospective utilization in nanotechnology, for example, for membrane nanoporation, biological material nanopatterning, template-based nanoimprint lithography, etc.

Surface NBs are capable to affect significantly interfacial processes including heterogeneous catalysis and electrochemical reactions on solid electrodes by blocking contact between solid and liquid phase, which in turn has serious impact to interfacial charge and mass transfer. Gaseous nanodomains are also expected to participate in transmembrane gas exchange.



**Figure 1:** Tapping mode AFM image of nanobubbles on polystyrene film immersed in water (A, in situ) and their imprint manifested ex-situ as nanoprotusion (B) and nanopinholes (C).

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# Observation of impregnating wetting behaviour of a liquid drop on hydrophilic patterned surfaces

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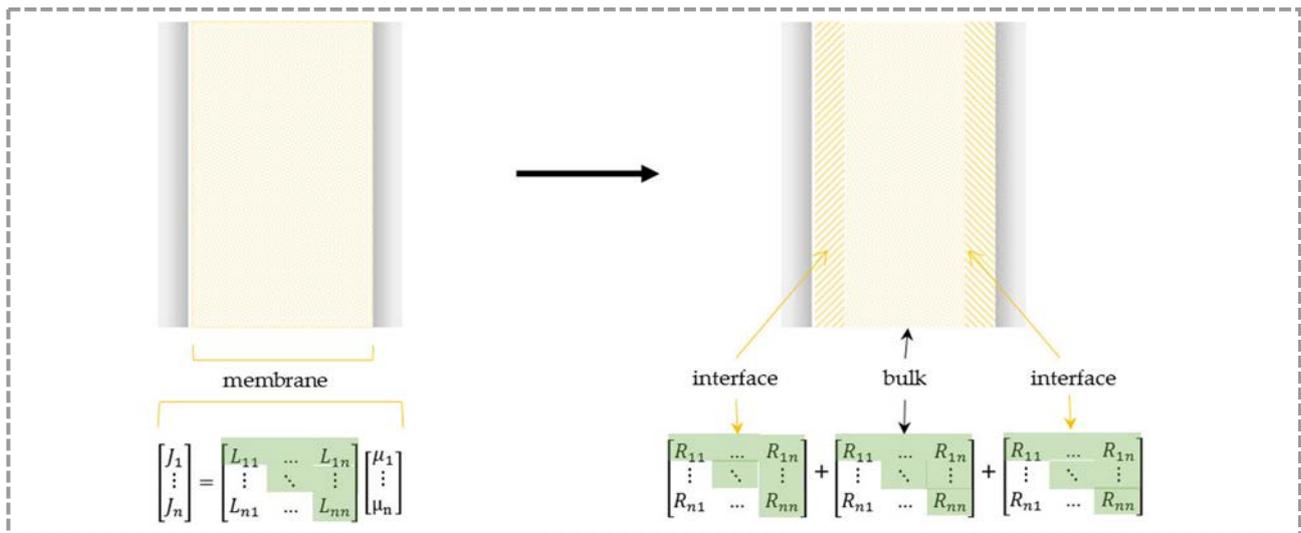
A series of regular pillar-like patterned PDMS surfaces with different surface roughnesses at a fixed solid fraction were fabricated to examine the wetting behavior of a liquid drop sitting on these patterned solventphilic surfaces. The advancing/receding contact angles were measured to verify whether a liquid drop sitting on the patterned solventphilic surface exhibits the Wenzel state or the Cassie impregnating wetting state. The wetting transition from the Wenzel state to the Cassie impregnating wetting state occurs on a surface with a certain surface roughness. In addition, those patterned surfaces with liquid drops exhibiting the Cassie impregnating wetting state were further applied to demonstrate the final shape of the wetted area during imbibition of the texture, e.g., octagons, squares and circles. The final shape of the imbibed area depends on the surface roughness. Under the condition of a fixed aspect ratio (ratio of the pillar height and pillar size) when the pillar distance decreases, a liquid drop would exhibit a transition from Wenzel state to the Cassie impregnation state. The final shape of the imbibed area would exhibit a series of transitions: square → octagon → circle in sequence. The relationship of the advancing/receding contact angles and the final shape of the wetted area was also discussed.

# Transport in Proton Exchange Membranes for Fuel Cell Applications – A systematic non-equilibrium approach

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We hypothesize that the properties of proton-exchange membranes for fuel cell applications cannot be described unambiguously unless interface effects are taken into account. In order to prove this, we first develop a thermodynamically consistent description of the transport properties in membranes, both for a homogeneous membrane and for a homogeneous membrane with two surface layers in contact with electrodes or holder material. For each subsystem, homogeneous membrane and the two surface layers, we limit ourselves to 4 parameters as the system as a whole is considered isothermal here. We subsequently analyze the experimental results on some standard membranes as have appeared in the literature and analyze these using the two different descriptions. This analysis yields relatively well-defined values for the homogeneous membrane parameters and estimates for those of the surface layers and hence supports our hypothesis.

As demonstrated, the method as used here allows for a critical evaluation of literature values. Moreover, it allows for a description of stacked transport systems such as proton-exchange membrane fuel cell units where interfacial layers, such as between catalyst and membrane, are taken into account.

**Acknowledgements** The financial support of the Advanced Dutch Energy Materials (ADEM) Program and the COST CM1101 Action is acknowledged.

# Depletion interaction in colloidal dispersions: controlled attractions?

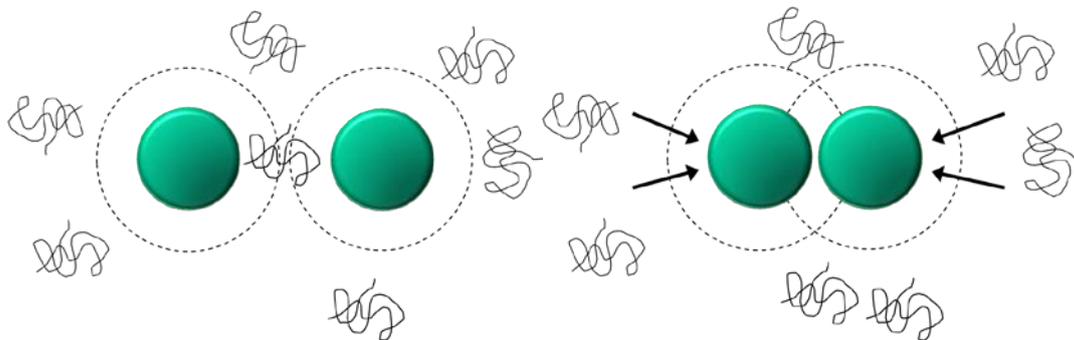
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The depletion interaction between colloidal particles mediated by nonadsorbing polymers is often identified as the tool to induce a controlled, tunable (strength and range of the) attraction between particles [1]. In this contribution it is shown, however, that depletion effects should be treated with care and are not as controlled as often assumed. First, it is demonstrated that the effective depletion interaction cannot be treated as pairwise additive due to the multi-overlap of depletion zones [2]. As a result, the general law that the second virial coefficient at the critical point is minus 6 times the particle volume [3] is violated. Secondly, the widely used assumption that the polymer segment is zero ('full depletion') at the colloid surface may often not hold, as illustrated using self-consistent mean-field computations and experimental examples (a recent one is [4]). It is shown that when the polymers are slightly adhesive to the colloidal surfaces, a weaker depletion effect is operational [5], and that the situation that the polymer segment concentration exactly vanishes at the surface is actually a rare case.



**Figure 1** Sketch of the attraction between two colloidal spheres mediated by nonadsorbing polymers.

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# Emulsification Kinetics: Assessing the intertwining roles of oil viscosity and interfacial tension

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The combined effect of viscosity ratio and interfacial tension on the process of emulsification is evaluated. For that, emulsification by ultrasonication of oil/water systems with viscosity ratios between 1 and 600, with and without surfactant was performed. The time evolution of the mean droplet size was evaluated by dynamic light scattering measurements. From the kinetic curves we found two major results: (1) A U-type curve of the final droplet size at viscosity ratios between 1 and 200 in presence of surfactant, similar to those reported in literature. Beyond that range, the droplet size decreases, as the viscosity ratio rises and interfacial tension diminishes. For surfactant free systems, the size is slightly affected by the increase of viscosity. This complex scenario is analyzed in terms of a recently proposed model by Gupta *et al.* [1], where both interfacial tension and viscosity ratio act on the emulsification process in a simultaneous and role-swapping way. (2) Systems with high viscosity and high tension reach a final mean size value lower than the same system without surfactant. Based on that, it is proposed that the emulsification of high viscosity oils could be improved by a retarded addition of surfactant.

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# Mechanical analysis of particle interactions and their effect on the macroscopic response of nanoparticle assemblies

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The mechanical behavior of nanoparticle assemblies depends on particle interactions that are difficult to study experimentally. In this research, it is intended to study these interactions through a numerical simulation in order to determine their effect on the mechanical properties of the formed structures. To achieve this purpose, a cyclic simple shear test was modeled using the Discrete Element Method (DEM). Starting from doublet interaction, we evaluate the effect of individual parameters on the contact forces. Consequently, the system is extended to the ensemble of particles where multibody interaction becomes dominant. This simulation consisted of a group of nanoparticles which are exposed to shear flow while considering three different types interactions, i.e. hard, frictional and adhesive contacts. For each case, mechanical properties such as Stiffness coefficient and Maximum shear stress were calculated from simulated force-displacement curves. Results exhibited that friction and adhesion have a direct influence on the stiffness of the system, depending on how close the particles are. Particularly, it is observed that the predominant forces during the doublet simulation vary depending on the range particle interpenetration, which is directly related to the overall stress applied to the system. Indeed, for a surface energy of  $12 \times 10^{-3} \text{ mJ m}^{-2}$  it is observed that adhesive force is dominant from an interpenetration distance of 0 to 0.001 times the particles radius (R). After, friction force starts to overcome adhesive force until a distance of  $0.18 \times R$ , where friction force is dominant and no effect of adhesion is observed. Regarding to the Stiffness coefficient, the value obtained from an assembly of adhesive particles was higher than the one obtained from the assembly which considers only frictional contact model; while the frictional contact model resulted in an increase of the Shear modulus with respect to the hard contacts model. Thus, it is verified that changing the type of contact interactions directly influences the macroscopic mechanical response of the nanoparticle assembly. The methodology used in this work presents an alternative way to predict the mechanical behavior of nanoparticle systems. Moreover, it allows optimizing it by adjusting primary particle properties.

**Acknowledgements** The financial support of Grant Agency of Czech Republic (Grant No. 16-22997S) is greatly acknowledged.

# HOW COSOLUTES STABILIZE MACROMOLECULES: FROM BRIDGING TO DEPLETION ATTRACTION

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Solution composition is known to strongly influence the stable state of macromolecules, with important practical applications ranging from colloidal dispersions to solvated polymers or proteins. Cosolutes with different affinities to specific macromolecular states can shift equilibrium towards the thermodynamically preferred state with lower free energy. Solutes preferentially excluded from macromolecules drive depletion forces and stabilize the compact macromolecular state. To contrast, cosolutes preferentially included around the macromolecule usually destabilize the compact state, effectively stabilizing the extended state of the macromolecule, as in the case of protein denaturants. However, in certain cases preferentially included cosolutes stabilize another compact state through bridging interactions. By using a simple mean field model that contains only few interaction parameters, we demonstrate the possible mechanisms by which preferentially interacting cosolutes affect macromolecules. Specifically, depletion interactions, bridging stabilization, and macromolecular destabilization, all emerge in a single model as concentration, interaction parameters, and cosolute size are varied. The theory also highlights the possible sources of energetic and entropic contributions to stabilization.

# Incorporation of ion structure into Poisson-Boltzmann theory

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Electrostatic interactions between charged objects in electrolyte solutions are of fundamental importance in colloid and surface chemistry [1,2]. Small mobile ions of an electrolyte interact with a charged object and an electric double layer is formed. The competition between electrostatic attraction and translational entropy loss of the ions can be modelled within the classical Poisson-Boltzmann theory. This theory ignores correlations and steric effects; the aqueous solution is described as a uniform dielectric continuum with a given dielectric constant. In this work, we focus on structural details of the ions, which include excluded volume effects and the presence of charge distributions on individual ions, spatially extended ions [2,3,4]. We showed that the theory predicts a saturation of large ions close to the highly-charged surface. Multivalent ions with spatially distributed charge can induce attraction between like-charged objects. The attraction results from inter-ionic correlations [1].

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# Effect of rotational diffusivity on the clustering of self-propelling colloids

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In equilibrium, colloidal suspensions governed by short-range attractive and long-range repulsive interactions form thermodynamically stable clusters. Using Brownian dynamics computer simulations, we investigate how this equilibrium clustering is affected when such particles are self-propelled. We find that the clustering process is stable under self-propulsion. For the range of interaction parameters studied and at low particle density, the cluster size increases with the speed of self-propulsion (activity) and for higher activity the cluster size decreases, showing a non-monotonic variation of cluster size with activity (Fig. 1A). This clustering behavior is distinct from the pure kinetic (or motility-induced) clustering of self-propelling particles which is observed at significantly higher activities and densities. We present an equilibrium model incorporating the effect of activity as activity-induced attraction and repulsion by imposing that the strength of these interactions depend on activity superlinearly. The model explains the cluster size dependence of activity obtained from simulations semi-quantitatively.<sup>1</sup>

In addition to the dependence of activity on the cluster size, we find that rotational diffusivity also plays a role in determining the mean cluster size. We examined the clustering evolution in the system for the density of 0.13 and for rotational diffusivities in the range of 0.01 to 30. In this range of rotational diffusivities, the cluster size shows a non-monotonic variation with activity by first showing an increasing trend followed by a decreasing trend (Fig. 1A). The critical activity required for the onset of dissolution of clusters increases with rotational activity. However, at higher diffusivities, the maximum cluster size is not very different from the cluster size obtained in passive particles. The study illustrates the complex interplay of inter-particle interactions, activity and rotational diffusivities on the mean cluster size.

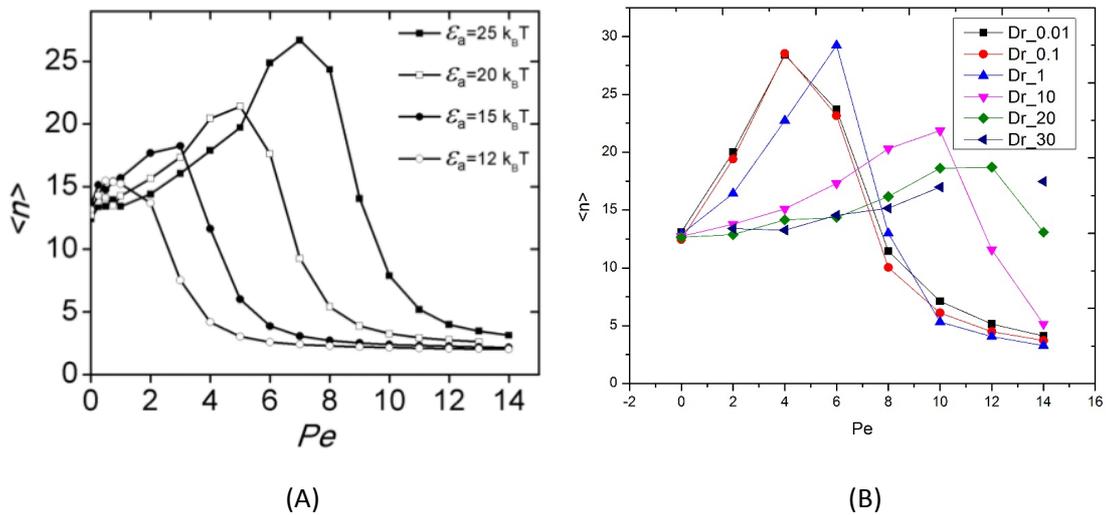


Figure 1. Mean cluster size as a function of activity for different (A) interaction energy parameter and (B) rotational diffusivity

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# Control over phase synchronisation in rotor models of motile cilia

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The coordinated cyclic beating of eukaryotic cilia and flagella is responsible for vital functions such as motility of microorganisms and fluid transport close to various epithelial tissues. Synchronization induced by hydrodynamic interactions is a possible and potentially general mechanism behind this coordinated beating of cilia. Simple models are required to gain a quantitative understanding of these systems, and as a first step one must disentangle the two scales in these systems: phenomena within and between cilia. Non-linear and non-thermal effects are present at both scales.

We focus here on a model that is tractable analytically and can be realized by optical trapping of colloidal particles, where the intra-cilia properties are coarse grained into the parameters chosen to drive the particles around closed orbits [1,2]. We study how, depending on these effective parameters, a variety of different phase-locked steady states can be achieved inter-cilia demonstrating that modest tuning of the cilia beating properties, as could be achieved biologically by modulation the molecular motor activity or binding affinity, or the cilia length and orientation, can lead to dramatic changes in the collective motion that arises out of hydrodynamic coupling. The experimental results are consistent with Brownian dynamics simulations and analytical calculations that includes the modulation of the driving force and the hydrodynamic interaction [3].

**Acknowledgements** –We acknowledge the financial support of ERC (*HydroSync* project), and AM to a Royal Society Newton International Fellowship.

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# Directed percolation: an equilibrium pre-transition towards non-equilibrium arrested gel states

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The macroscopic properties of gels arise from their slow dynamics and load bearing network structure, which are exploited by nature and in numerous industrial products. However, a link between these structural and dynamical properties has remained elusive. In this contribution [1] I will present confocal microscopy experiments and simulations of gel-forming colloid-polymer mixtures. They reveal that gel formation is preceded by continuous and directed percolation. Both transitions lead to system spanning networks, but only directed percolation results in extremely slow dynamics, ageing and a shrinking of the gel that resembles syneresis. Therefore, dynamical arrest in gels is found to be linked to a structural transition, namely directed percolation, which is quantitatively associated with the mean number of bonded neighbours. Directed percolation denotes a universality class of transitions. Our study hence connects gel formation to a well-developed theoretical framework, which now can be exploited to achieve a detailed understanding of arrested gels.

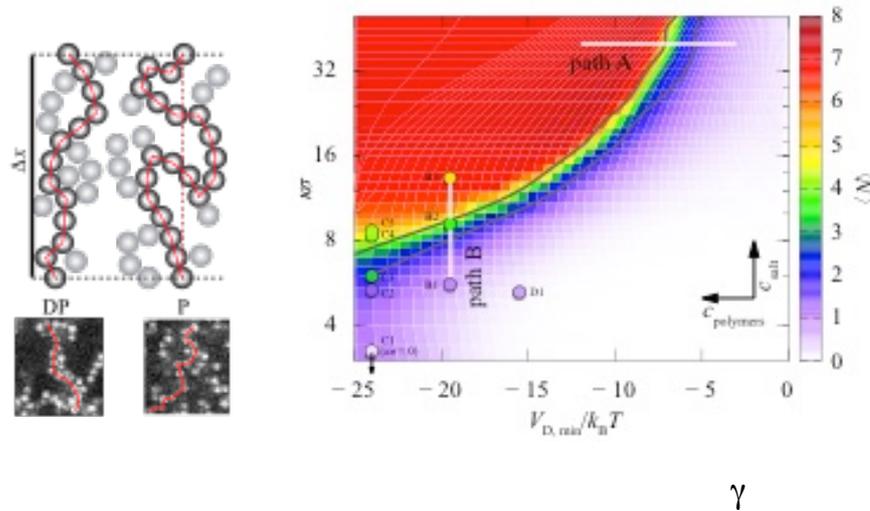


Figure 1: Left: Sketch (top) and confocal microscopy images (bottom) illustrating the difference between percolation (P) and directed percolation (DP) in a gel structure. Right: State diagram illustrating the relation between directed percolation and gelation.  $\langle N \rangle$  is the average number of neighbors,  $V_{D,min}$  is the depth of the potential well,  $\kappa\sigma$  represents the degree of screening of the electrostatic interaction (hard-sphere interactions are recovered in the limit of large  $\kappa\sigma$ ). The red region represents gels and is delimited by the directed percolation line. The paths indicated were investigated by simulations and experiments.

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# Active Hybrid Supraparticles Containing Microfibrillated Cellulose [MFC]

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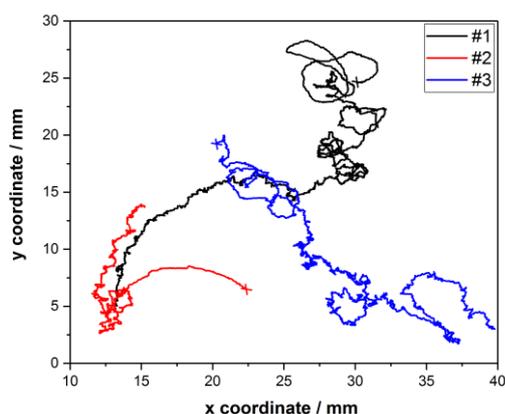
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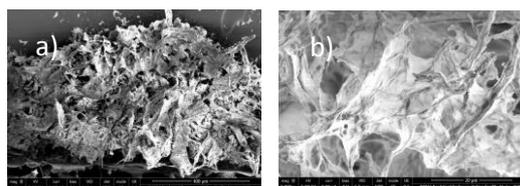
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In this project, hybrid supraparticles of microfibrillated cellulose (MFC) and fumed silica (FS) were prepared on superhydrophobic surfaces by means of evaporation induces self-assembly (EISA). By being biocompatible and highly porous, MFC is a promising component to be used in active particles for biomedical or catalytic applications. The other component FS has also wide variety of applications due to its properties such as large surface area, functionality and stability. By changing the ionic strength of the initial solutions, it was possible to control the anisometry of the particles in a systematic fashion, going from spherical to elongated supraparticles [2].

Our motivation was to use these sub-millimeter anisometric particles to obtain tunable self-propulsion. The self-propelling properties were imparted by adding Pt-covered magnetite (Pt@Fe<sub>3</sub>O<sub>4</sub>) nanoparticles to the colloidal suspension and concentrate them on a pre-determined location as a patch, which was possible by doing the preparation on an indented surface which allows controlling the elongation direction of the supraparticles. In this way, supraparticles were obtained with both, magnetic and catalytic properties, which enable self-propulsion with a suitable fuel and the steerability by a magnetic field. The trajectories of these boat-like supraparticles were studied by means of videomicroscopy as a function the shape of the supraparticles, the position of the catalytically active patch, and the concentration of the fuel. From these studies systematic correlations between these parameters and the observed trajectories could be deduced, where in particular the extent of anisometry of the supraparticles has a profound effect.



**Figure 1** Trajectories of 3 particles.



**Figure 2** SEM micrographs of freeze-dried MFC based patchy particle (Magnification a: 120x, b: 2000x).

## Acknowledgements DAAD & IRTG 1524

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# Ultrasensitive Colorimetric Detection of the Earlier Stages of Metallic Corrosion Using Plasmonic Gold Nano-Islands

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Corrosion is a natural process of degradation of metallic materials due to a reaction with their environment and is the major reason for the metallic parts failure in-service. Hence, detection of the earlier stages of metal parts oxidation is of great importance. Here we show a facile colorimetric method for monitoring the surface condition of aluminum using the localized surface plasmon resonance response of noble metal nanoparticles pre-deposited onto the Al surface. Upon oxidation, metallic aluminum transforms to completely transparent dielectric aluminum oxide. In water the formed oxide layer adopts a two-layer structure; the bottom layer is thinner and compact, while the top layer is thicker and highly porous. The gold nano-islands, deposited on top of aluminum, after oxidation in water are confined in between the two aluminum oxide layers. Moreover, the oxidation leads to pronounced color change, which can be monitored *in situ* in reflection spectroscopy or colorimetrically by bare human eye. Theoretical calculations show that the major spectral change in such system occurs due to light interference within the bottom aluminum oxide layer, which is acting as an etalon sandwiched between the Au islands and the underlying Al. The top aluminum oxide layer, which is porous and diffuse, has minor contribution. This work demonstrates that the plasmonic nanoparticles in general and nano-islands in particular are well suited for real-time monitoring of corrosion kinetics of metals in almost any environment. The technique is cost-effective in terms of the equipment and can be applied in both transmission and reflection measurement modes.

# Future food structuring technologies at micro- and nanoscale

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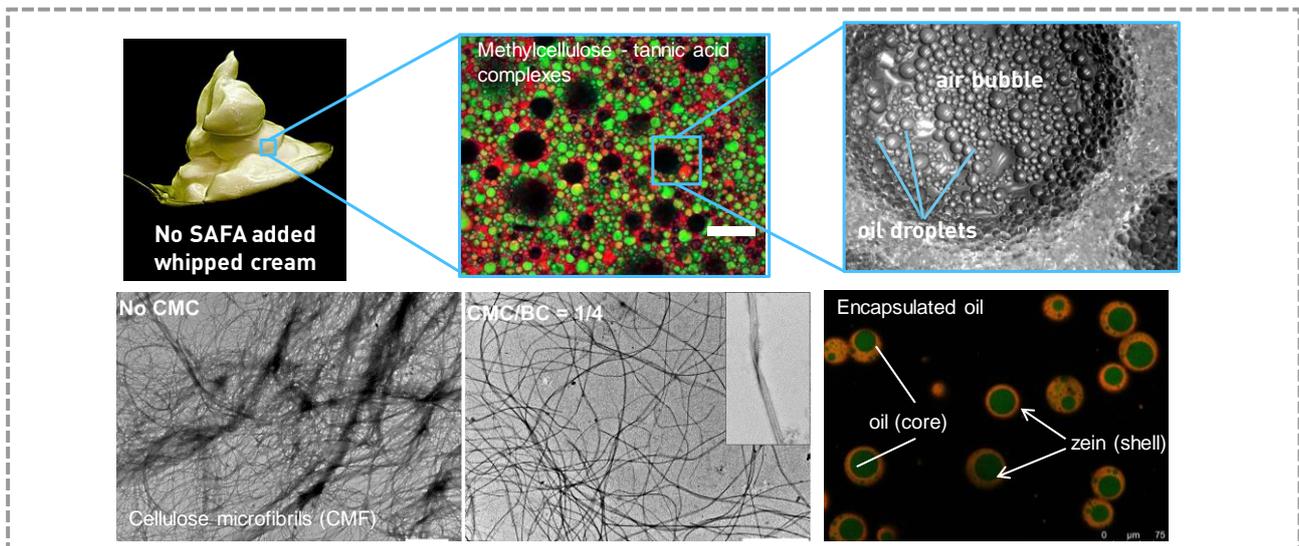
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Food industry is driven by a strong demand for high quality products with no health concern that contain sustainably sourced natural ingredients. This creates several challenges related to our ability to build consumer perceived differentiating textures with current ingredients. The introduction of new ingredients is strongly limited by safety and consumer perception. To address these challenges, we generally need a better control of consumer relevant product functionality (i.e. appearance, taste, texture, stability) by applying better control over existing structures and ingredient interactions. This could be achieved by alternative or novel uses of existing materials and their interactions. Another approach is to further unlock the potential of underutilized natural materials (e.g. cellulose, insoluble plant proteins) to build new architectures. Novel uses of ingredients (e.g. emulsion stabilization by non-surface active molecules) or exploring unwanted interactions to create useful structures are other potential approaches. Nano-scale control of interactions and structures can be used for more effective use of materials. Finally, control of structure breakdown based on known digestion and physiological effect on new structures is necessary to assure full utilization of nutrients and micronutrients. In this talk, several examples of such approaches from program **5B Molecular Structure of Food** in **NanoNextNL** will be discussed. These will include utilization of strong molecular interactions, cellulose microfibrils, and water insoluble plant proteins.



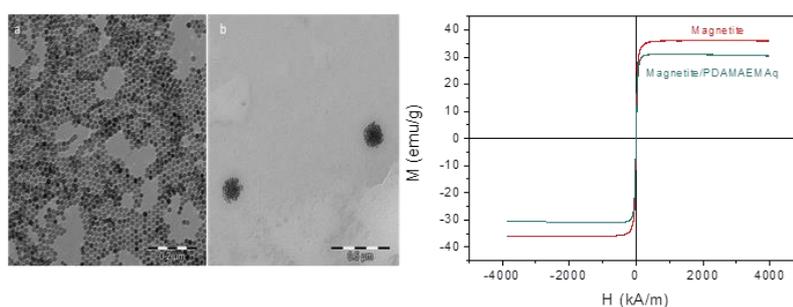
**Acknowledgements** This research is financially supported by NanoNextNL (consortium of Dutch government and 130 other partners).

# Novel smart polymer-coated magnetite nanoparticles with hyperthermia properties

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Syntheses of magnetic nanomaterials with temperature responsive properties have been described previously by incorporating magnetic cores into thermosensitive polymers, such as poly(N-isopropylacrylamide) (PNIPAAm) [1]. Poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) is another thermosensitive polymer rarely used as part of a magnetic carrier, but it is known to have very interesting properties. The quaternary ammonium salt (PDMAEMAq) of this polymer possesses additionally antimicrobial properties, water solubility and hydrophilicity below the low critical solution temperature (LCST), while above it, the chains undergo a sharp coil-to-globule transition that results in hydrophobic and insoluble aggregates [2]. This research work describes the synthesis of magnetite nanoparticles prepared by a hydrothermal, high temperature method, followed by a phase transfer to aqueous media (Figure 1a-1b). These nanoparticles were coated with PDMAEMAq using a simple emulsion step, reducing the amount of purification steps, decreasing the preparation time and avoiding sophisticated synthesis conditions. The existence of the polymer coating was confirmed by TEM, DLS, zeta potential and thermogravimetric measurements. The particle increased to 98 nm when the PDMAEMAq coated the magnetic core. In aqueous medium at pH7.4 the zeta potential was -42 mV before adding the polymer coating and it changed to -13 mV after coating with the positive charges of PDMAEMAq. These nanoparticles showed a LCST around 40 °C at a physiological pH. The magnetization values before coating showed a saturation value of 36 emu/g, which was reduced to just 32 Oe/g when PDMAEMAq coated the magnetic core (Figure 1c). Both of them showed a clear absence of hysteresis. The hyperthermia response of these nanoparticles was measured at 110 kHz with a maximum current of 7A, and we found a heating rate of 10 °C/min for a 0.5 mL sample containing 1 % particle concentration, which makes these magnetic nanoparticles suitable for cancer diagnosis and treatment applications.



**Figure 1.** TEM images of magnetite nanoparticles in organic phase (a), and coated with PDMAEMAq in aqueous phase (b). Room temperature magnetization curves of both nanoparticle systems (c).

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**Acknowledgements** The financial support of Junta de Andalucía, Spain (project PE2012-FQM694) is gratefully acknowledged.

# Elaboration of functionalized titania nanosheet based nanocarriers for antioxidant applications

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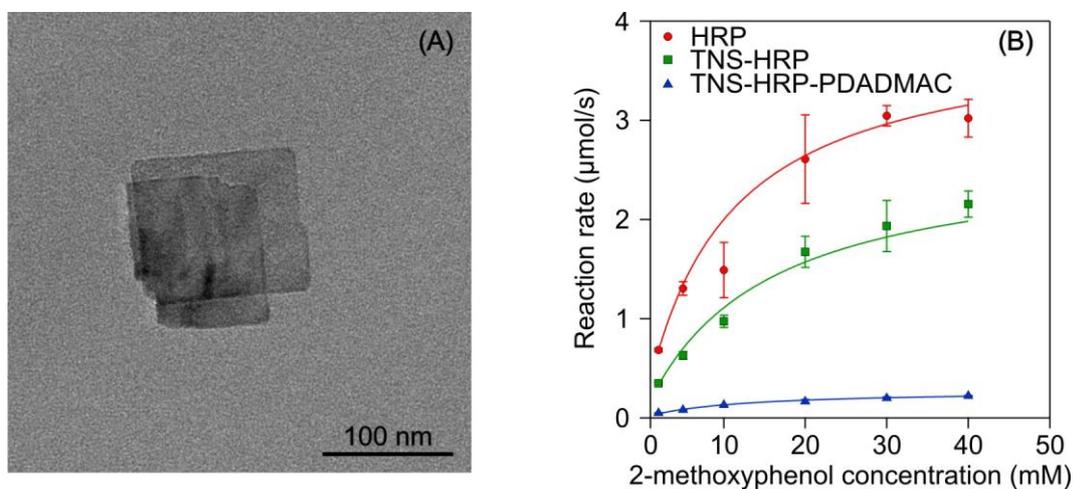
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Enzymes or enzyme based materials are receiving considerably more interest as their applications in various fields (e.g. chemical manufacturing processes, biomedical treatment) have been growing. Among the different classes of enzymes, antioxidant enzymes are of particular importance as they convert reactive oxygen species (ROS) into oxygen and water [1,2]. However, enzyme efficiency is highly affected by the medium such as the pH, ionic strength and temperature. In order to increase reusability and functional stability of the enzymes, their immobilization on solid supports appears to be a promising approach [3].

We have investigated antioxidant systems based on titania nanosheets (TNS) functionalized with horseradish peroxidase (HRP) enzyme. Enzyme immobilization on the nanomaterials occurred through electrostatic and hydrophobic interactions. To prevent any leakage of the immobilized enzyme from the support and to further protect it from the external medium, polyelectrolyte functionalization of TNS was performed. Depending on the polyelectrolyte dose applied, charge neutralization and overcharging were observed. Charge neutralization of the particles resulted in unstable dispersions while charge reversed particles form stable suspensions, where primary particles (Figure 1A) were observed.

Finally, the enzymatic activity (Figure 1B) of the functionalized nanomaterials were determined and compared to the native enzymes.



**Figure 1.** (A) Transmission electron microscope image of a coated TNS. (B) Enzymatic activity of HRP, immobilized HRP on TNS (TNS-HRP) and TNS-HRP functionalized with poly(diallyldimethylammonium chloride) (PDADMAC) (TNS-HRP-PDADMAC) on the degradation of 2-methoxyphenol.

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# Simultaneous encapsulation of bioactive components for nutrition and plant protection

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Novel chitosan/alginate microcapsules simultaneously loaded with copper ions and *Trichoderma viride* have been prepared and characterized. Information about intermolecular interactions between biopolymers and bioactive agents were obtained by Fourier transform infrared spectroscopy. Encapsulation of *Trichoderma viride* spores and the presence of copper ions in the same compartment do not diminish their activity [1].

Dependence of microcapsule loading capacity and efficiency, swelling behavior and releasing depends on both, the size of the microcapsule and bioactive agents. The in vitro copper ions release profile was fitted to Korsmeyer–Peppas empirical model. Fickian diffusion was found to be a rate-controlling mechanism of release from smaller microcapsules, whereas anomalous transport kinetics controlled release from larger microcapsules. *Trichoderma viride* spores releasing profile exhibited exponential release over the initial lag time. Results obtained opened up perspectives for the future use of chitosan/alginate microcapsules simultaneously loaded with biological and chemical agents in the plant nutrition and protection [2].

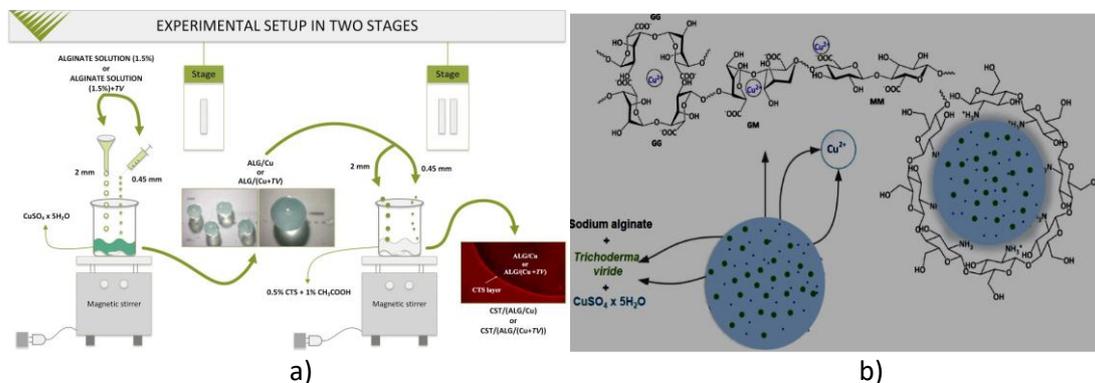


Figure 1. a) Schematic diagram of the experimental setup corresponding to ionic gelation (the first stage-I) and polyelectrolyte complexation (the second stage-II) and b) schematic presentation of core microcapsule formation in the first stage and formation of chitosan layer in the second stage.

**Acknowledgements** The financial support of Croatian Science Foundation

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# Structure-activity relationships governing the efficiency of antioxidants in multiphasic systems: tuning interfacial concentrations

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The efficiency of antioxidants (AOs) in inhibiting lipid oxidation depends on several factors including the nature of the AO and their concentration at the reaction site. Chemical modifications of the reactive moieties to modulate their efficiency are not always possible because of the inherent experimental difficulties and because of the regulatory status of AOS cannot be ignored when selecting antioxidants for use. An alternative approach to modulate the AO efficiency is to use of potent, natural, antioxidants and modify their hydrophobicity so that their reactive moiety is maintained but their HLB is chemically modified by insertion of, for instance, alkyl chains of different length. This strategy exploits the changes in their relative solubility in the distinct regions of the emulsions as a consequence of the changes in their hydrophilic-lipophilic balance (HLB) of the AOs, leading to changes in their concentrations at the reaction site (the interfacial region of emulsions). For the purpose we synthesized series of AOs derived of potent, natural AOs such as hydroxytyrosol or caffeic acid, bearing the same reactive groups but of different hydrophobicity.

Here we report on the effects of series of homologous AOs on the oxidative stability of intact oil/water/tween 20 emulsions by monitoring the formation of conjugated dienes (CDs) at early stages of oxidation. Their relative efficiency was evaluated as the time required to increase the amount of conjugated dienes, CDs, after the propagation step of the radical reaction is reached. To rationalize the results, we determined their distributions and interfacial concentrations in the same intact emulsions.[1-3]

Results show that the efficiency of several series of homologous AOS does not increase linearly with increasing the number of C atoms in their alkyl chain but is parabolic-like, with a maxima at an intermediate (C4 – C12) chain length. This parabolic dependence of AO efficiency upon chain length for both chemical and biological activities of series of homologous AOs up to a critical point after which their activity decreases is known as the “cut-off” effect. Results illustrate an effective and convenient way to control lipid oxidation by modulation of the hydrophobicity (HLB) of the AOs and provide physical evidence that the variations in the efficiency of homologous series of antioxidants in emulsions are due to differences in their interfacial concentrations, confirming that - other things being equal - there is a direct relationship between the percentage of AO in the interfacial region of the emulsions and their efficiency. An increase in the alkyl chain length of the AOs promote their incorporation into the interfacial region of emulsions but only up to a critical chain length, after which a further increase makes their efficiency to decrease as a consequence of the decrease in their %AOI. Application of the pseudophase kinetic model furnishes, therefore, a natural explanation, based on molecular properties, to the cut-off effect.

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# Diffusive interaction of multiple surface nanobubbles

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Xiaojue Zhu<sup>1</sup>, Martin van der Hoef<sup>1</sup>, Xuehua Zhang<sup>3,1</sup>

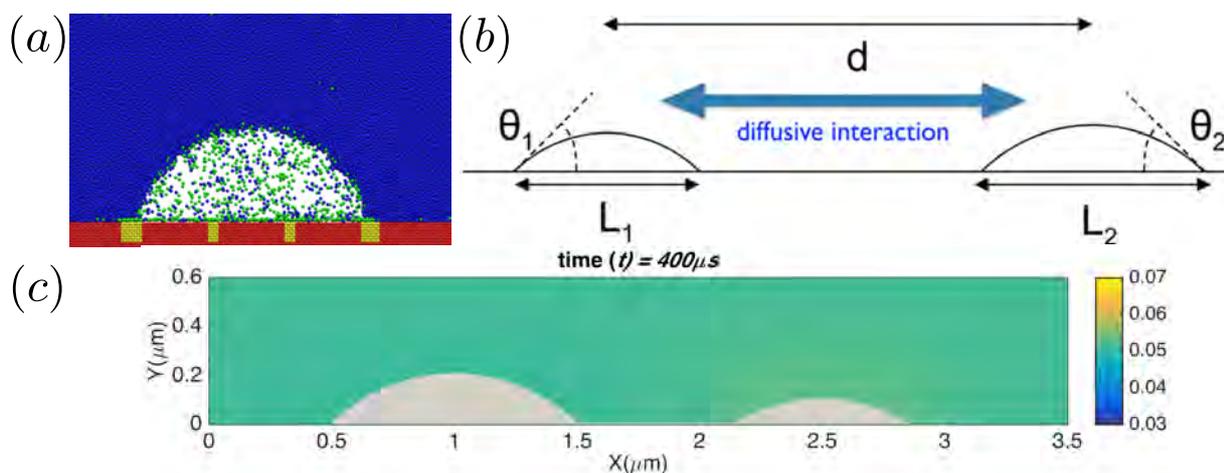
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Surface nanobubbles are nanoscopic gaseous domains on immersed substrates which can survive for days. After existence and the stability of a single surface nanobubbles has been clarified – namely contact line pinning and gas oversaturation are required to stabilize them against diffusive dissolution [1] - we now focus on the collective diffusive interaction of multiple nanobubbles, their analogy to nanodroplets, their formation and growth process through solvent exchange, and their dissolution in gas-undersaturated water. In particular, we theoretically show that the pinning also suppresses the Ostwald ripening process between neighboring surface nanobubbles [2]. These findings are supported by molecular dynamics simulations [3] and by finite difference simulations of the diffusion equation with the appropriate boundary conditions and with the immersed boundary method used to represent the growing or shrinking bubbles [4]. The framework of these simulations is also used to describe the coarsening process of competitively growing nanodroplets such as experimentally observed in [5]. We observe and quantify the coarsening process of the growing droplets, either through Ostwald ripening or through coalescence.



**Figure 1** (a) MD simulation of a surface nanobubble on a chemically structured surface in gas-oversaturated solution, demonstrating the stability of the surface nanobubble. From [3]. (b) Schematics of diffusive interaction of two surface nanobubbles. From [2]. (c) Finite difference simulation of diffusion equation with immersed boundary method, showing the stability of two surface nanobubbles. From [4].

**Acknowledgements:** DL acknowledges financial support by an ERC-Advanced Grant and by the Max Planck Twente Center on Complex Fluid Dynamics.

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# Anisotropic spreading along the textured surfaces with isotropic wetting

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In recent years, one of the most intensively developed areas in physical chemistry of functional materials is the creation of coatings with the ultrafast spreading of a number of liquids along the surface of coatings with the formation of uniform wetting layers. Designing such surfaces is a complex scientific and technical problem. The surfaces with multimodal roughness based on nano- and microelements of the texture, which are chemically modified to improve wetting with test liquids are considered as the most promising for achieving this goal.

In this paper, we propose methods for obtaining such surfaces based on nanosecond laser texturing, and describe a setup developed for detailed investigation of ultrafast spreading of liquids. The regularities of spreading of the precursor layer of the decane and silicone oil on surfaces having the same texture but with different chemical treatments were studied. It is shown that for such surfaces the contact angles are independent of direction whereas wetting hysteresis is anisotropic. We have revealed the anisotropy of spreading over such surfaces and the influence of fluid volatility on the spreading process.

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# Wetting over pre-existing liquid films – a tsunami on microscale

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Wetting of solids by liquids is a ubiquitous phenomenon of our everyday life. It governs the fundamentals for several industrial operations including spray-, dip- or cast-coating, heat transfer, and water harvesting [1-3]. Wetting is determined by the interplay of surface tension, gravity, viscous stresses, and inertia. So far, wetting research has focused on modeling of drops or liquid streams on solid or elastic substrates [4,5]. Little is known about the motion of a liquid over another, pre-existing liquid film. This is due to the lack of space and time resolved techniques, which can discriminate between the two liquids. Here we resolve the spreading dynamics of silicone oil meniscus over a thin film of the same liquid in 3D using laser scanning confocal microscopy. When the meniscus rests on a smooth surface, strong capillary suction induces local thinning of the film. When moving forward, the viscous forces start to deform the liquid interface, giving rise to a wave-like film profile with local backflows. Apart from technical surfaces, such a “micro-tsunami” also takes place on the cornea of human eye [6].

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# Interaction of super-chaotropic ions with proteins

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The main focus of this study has been to investigate how different proteins interact with big organic ions (Ph<sub>4</sub>B<sup>-</sup> anion and Ph<sub>4</sub>As<sup>+</sup> cation) [1]. These hydrophobic ions have been classified as super-chaotropes due to their great interaction with hydrophobic interfaces [2]. The proteins used in this study are the two major allergenic proteins of cow's milk, β-lactoglobulin and β-casein, and bovine serum albumin, BSA, as the reference protein. Understanding the protein–ion interaction is important from a fundamental point of view as well as for the numerous applications where proteins are involved. For instance, the presence of ions is very relevant in the food industry (formation and stabilization of emulsions) or biosensor applications, among others [3]. First, a quantitative study to determine the hydrophobic degree of the proteins was performed. Then, electrokinetic and stability studies on protein-coated polystyrene microspheres and quartz crystal microbalance (QCM) measurements on protein films as a function of the tetraphenyl ion concentration were carried out. All the results evidence that the accumulation of these organic ions on an interface depends directly on its degree of hydrophobicity [2,4]. On the other hand, we have analyzed the interaction of polyoxometalates (POMs) ions on our systems. These ions have a growing interest in various applications as catalysis, material science, electrochemistry, lithography, medicine, among others and they have been recently classified as super-chaotropes due to their great adsorption on different interfaces [5]. Our results show that POMs ions strongly interact with all the proteins interfaces. From the comparison of the results with the different ions, we revisit the meaning of super-chaotropic character of the ions.

**Acknowledgements** The authors wish to thank the financial support granted by the projects CTS-6270 (Junta de Andalucía, Spain), FIS2016-80087-C2-1-P and SEV-2015-0496 (Ministerio de Economía y Competitividad, Spain) and COST Action MP1303: Understanding and Controlling Nano and Mesoscale Friction.

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# Tracking of fluorescently labelled polymer particles reveals surface effects during shear-controlled aggregation

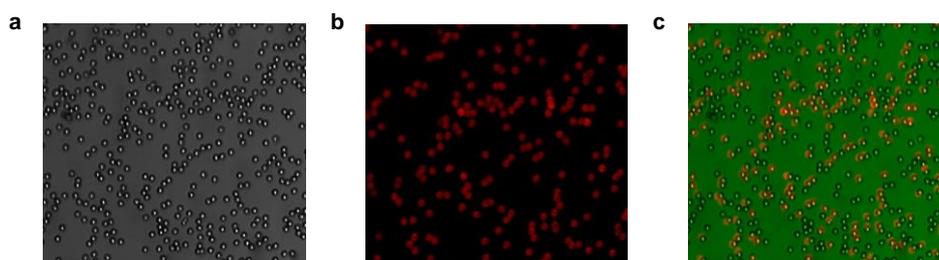
Stefano Caimi<sup>1\*</sup>, Alberto Cingolani<sup>1</sup>, Baptiste Jaquet<sup>1</sup>, Massimo Morbidelli<sup>1</sup>, Marco Lattuada<sup>2</sup>

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Surface chemistry is believed to be the key parameter affecting the aggregation and breakage of colloidal suspensions when subjected to shear. To date, only few works dealt with the understanding of the role of the physical and chemical properties of the particles' surface upon aggregation under shear. Previous studies suggested that surface modifications strongly affect polymer particles' adhesion, but it resulted very challenging to demonstrate this effect and monitor these alteration upon prolonged exposure to shear forces [1]. More importantly, the mechanisms leading to these changes remain elusive. Molecular dynamics simulations have highlighted the possibility of material transfer between particles as a result or repeated aggregation/breakage events [2]. Along this line, shear-induced aggregation experiments of polymer colloidal particles have been devised, with the specific objective of highlighting material transfer and clarifying the role of the softness of the particle's surface. To achieve this goal, polymer particles with a core-shell structure comprising of fluorescent groups have been prepared, so that the surface's softness could be tuned by addition of monomer acting as plasticizer and the percentage of fluorescent particles could be recorded over time via confocal microscopy to detect eventual material transfer among different particles. As a result of these experiments, for the first time, material exchange occurring on the soft surface of core-shell polymer micro-particles upon aggregation under shear was observed and proved. More aptly, starting from a 50% labelled/not labelled mixture, an increase in the percentage of particles showing a fluorescent signature was recorder over time, reaching after 5 hours a fraction of 70%.



**Figure 1:** Micrographs of the micro-particles in transmission mode (a), in fluorescent confocal mode (b) and their superposition (c).

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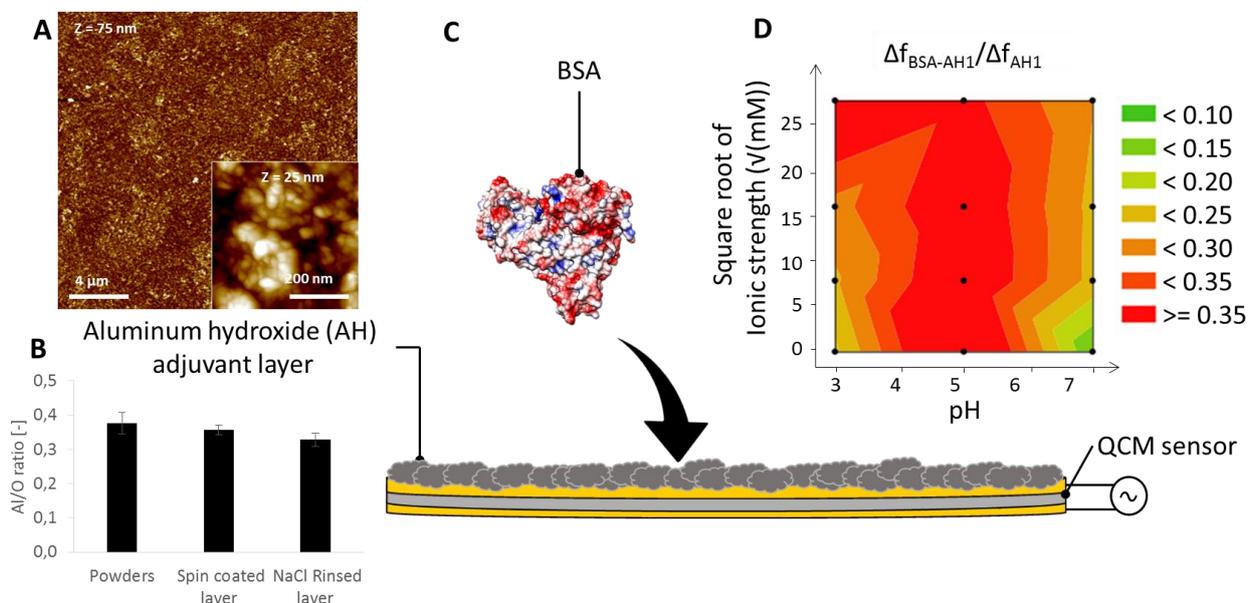
# Immobilization of aluminum hydroxide particles on quartz crystal microbalance sensors to elucidate antigen-adjuvant interaction mechanisms in vaccines

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**Aluminum hydroxide (AH) salts** are the most widely used adjuvants in vaccine formulation. They trigger immunogenicity from antigenic subunits that would otherwise suffer from a lack of efficiency. Previous studies focusing on protein-AH interaction mechanisms suggested that electrostatic interactions and phosphate-hydroxyl ligand exchanges drive protein adsorption. We however recently evidenced that NaCl, used in vaccine formulation, provokes AH particle aggregation. This must be taken into account to interpret data related to protein adsorption on AH. Here, we report on the successful development and use of a **stable AH-coated interface** to explore the mechanisms of **protein adsorption** by means of ultra-sensitive surface analysis tools (Figure 1). By studying bovine serum albumin (BSA) adsorption at different pH and ionic strength (I) via **Quartz Crystal Microbalance**, we show that protein adsorption on AH adjuvant cannot be explained solely by electrostatic interactions and ligand exchanges. Hence, a higher adsorption was observed at pH 3 compared to pH 7 while electrostatic interactions between AH and BSA are respectively repulsive and attractive at these pH values. Almost no effect of I on adsorption was moreover noted at pH 7. These new developments and observations not only suggest that another mechanism might regulate protein adsorption on AH, but also offer a **new platform for the study of antigen adsorption**.



**Figure 1.** A. Topographic image obtained by atomic force microscopy of AH particles spin coated on the surface of a QCM sensor after treatment with NaCl to stabilize the layer. AH particles keep their size and shape upon deposition. B. Surface chemistry of AH particles expressed as aluminium to oxygen ratio. Spin coated AH particles keep their original chemical composition. C. Scheme of the developed QCM platform, with BSA interacting with AH-covered QCM sensor. D. Map presenting BSA adsorption as a function of pH and square root of ionic strength, obtained through the use of the developed QCM method.

# A standardized routine for the determination of particle surface properties based on analytical centrifugation

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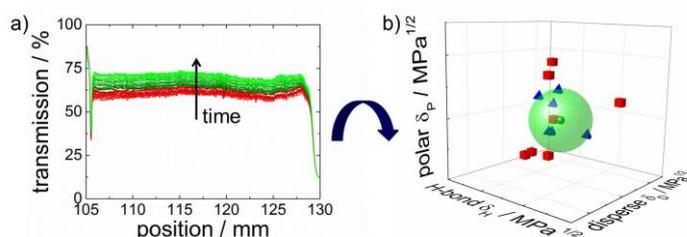
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For most particle-based applications, formulation in liquid phase is the decisive step. However, to obtain high-quality products, stable particles dispersed in liquids that suite to the requirements of the later application are mandatory. For particles smaller 100 nm the surface chemistry is of major importance, e.g. ligands bound to the particle surface. Hence, knowledge of particle interactions and stability in different liquids is necessary to adjust and improve the conditions for particle-based applications.

To measure colloidal stability as well as particle interactions, Hansen Solubility Parameters (HSP) can be used. HSP are based on the concept of Hildebrand-Parameter (HP), which are directly connected to the chemical potential and thus to the activity coefficient. To account for the origin of the interactions, HSP subdivide HP into disperse, polar and H-Bond contribution. Herein, a standardized and non-subjective procedure using analytical centrifugation (AC, LUMiSizer) was developed to determine HSP of nanoparticles (NPs). AC is a powerful method to characterize in situ the stability as agglomeration can be directly traced by sedimentation in a standardized AC experiment. If this procedure is repeated for a defined set of liquids with known HSP, good and poor media for NP dispersion are identified based on experimentally determined sedimentation times. Via HSPiP-software HSP are derived and colloidal surface properties become accessible.

First, a standardized procedure for the determination of sedimentation times and HSP was established and the well-known, technically relevant carbon black (CB, mean size 23 nm) was used as model system to obtain a procedure for derivation of HSP as material properties (Figure 1). To validate the developed approach, results were compared to expectations from literature. Reproducibility was demonstrated by comparing results obtained at different affiliations, LUM and FAU. The strength of the approach was shown by predicting the stability of CB dispersed in further untested liquids and liquid mixtures containing a beforehand good and poor ranked liquid. In the next step, the routine was applied to determine HSP of ZnO quantum dots (mean size below 5 nm), decorated with different catechol derivatives. With these, different surface polarities can be adjusted, whereat the HSP obtained in the presence of different chemisorbed functionalities highly fit to the expectations. This allowed analyzing size effects as well as the influence of the amount of catechol molecules bound to the particle surface. In conclusion, our work shows how colloidal surface properties are accessible by standardized and non-subjective routines using AC. With these, by knowing HSP of particles, determination of steric interaction potentials between ligands at the particle surface and surrounding liquid molecules is getting in reach.



**Figure 1** a) Sedimentation profile of CB dispersed in DMSO; b) HSP of CB as center of the green dispersibility sphere (green ball) around all good liquids (blue triangles) under exclusion of all poor liquids (red cubes).

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# Self-assembly, shape-selectivity and stability of chitosan/nanoparticle colloids by TR-USAXS

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Small-angle x-ray scattering (SAXS) is an established technique for characterizing systems across orders of magnitude.<sup>1</sup> Using beamline ID02 at the ESRF<sup>2</sup> we have probed the structure of a model chitosan/nanoparticle system across four orders of magnitude, and studied the self-assembly and structural evolution of the system on timescales between  $10^{-3}$  to  $10^7$  s (ms to two months).

When combined chitosan and silica nanoparticles exhibit a rich phase behaviour consisting of 1-D string-like clusters, 2-D and 3-D fractal complexes.<sup>3</sup> In resolving structural changes in the clusters both as a function of ionic strength, and over time we have been able to probe the microscopic drivers of the system.

The fast detectors, high-flux and unique flight-tube at ID02 enable examination of the kinetics of formation of the chitosan/nanoparticle clusters via stopped-flow on the micrometer, and millisecond scales. Cluster formation is dependent on the macroscopic properties of the system (silica surface charge, ionic strength) despite such properties having small effects on the stability of the system.

This work demonstrates that small-angle x-ray scattering can provide detailed structural and kinetic information even for multi-component complex systems with high polydispersity. Here SAXS provides a unique method of directly studying the thermodynamics of an out-of-equilibrium self-assembling self-stabilizing model system.

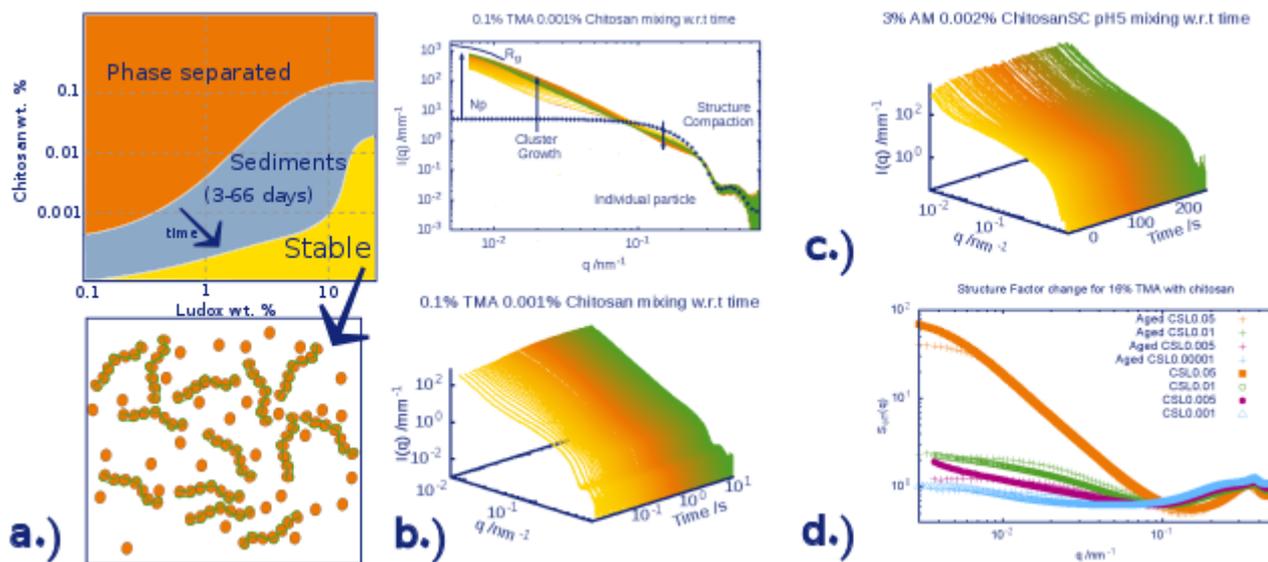


Figure 1: a) phase diagram of system; b) 2D and 3D plots demonstrating the self-assembly behaviour of the system; c) 3D plot indicating alternative self-assembly path; d) demonstration of the small changes in structure visible over 1 month

**Acknowledgements** The authors acknowledge provision of beamtime from the ESRF and support from the PSCM

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# Adsorption Morphology of Lipids on Graphene Surface

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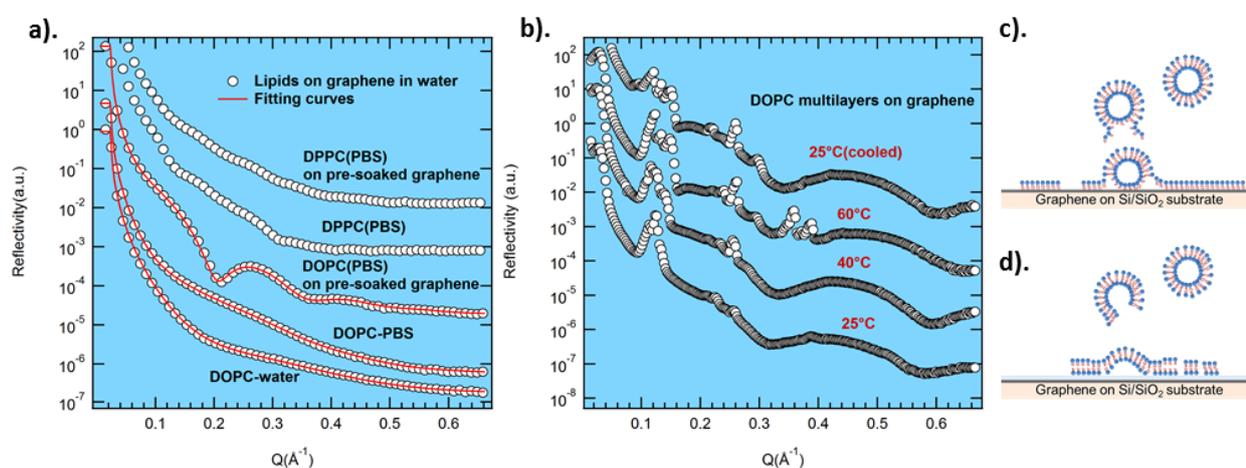
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Graphene, a two-dimensional monolayer of carbon atoms, is the basic building block of graphitic materials. Its unique physical properties make it one of the most popular materials in the world. Previous studies have shown its potential in bionanotechnology applications such as drug delivery, molecular imaging, and bio-sensing. However, the biocompatibility issue of graphene restricts its *in vivo* applications. Therefore, understanding the interaction of cell membranes and graphene surface becomes crucial for improving the biocompatibility of graphene.

Here we have chosen liposomes of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) and 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) to simulate cell membranes for this study. The structures of lipids membranes on graphene, prepared by the vesicle fusion method or drop casting, were studied using synchrotron X-ray reflectivity (XRR) at the European Synchrotron Radiation Facility. XPS, PEEM (photoemission electron microscopy) and AFM were used to evaluate the composition, morphology and the surface chemistry of the commercially available graphene substrates.

XRR results (Figure 1 below) show that the structure and thickness of graphene had changed after soaking in water for one day, thus leading to a different lipid adsorption structure on graphene. Increasing temperature within a certain range and the presence of phosphate buffer saline (PBS) also have influences on the adsorption of lipids. Additionally, the structure of the DOPC multilayers on graphene reversibly changed upon heating and cooling. Further interpretations on this phenomenon will be pursued for a more accurate model for the data analysis.



**Figure 1** a). Experimental XRR curves of lipids membranes on graphene prepared by the vesicle fusion method, collected in water or PBS at room temperature. b). XRR curves of DOPC multilayer from an SUV dispersion on graphene in air at different temperature. c) & d). The formation of lipid membranes on graphene by vesicle fusion method.

**Acknowledgements** Financial support of Procter & Gamble and MCITN NanoS3; Synchrotron X-ray access at ESRF CRG XMAS beamline and the support by the beamline staff; Soft Matter at Interface group for support during XRR measurements.

# Colloidal Microcapsules for Dual Drug Delivery

Nihal Aydoğan<sup>\*</sup>, Gokce Dicle Kalaycioglu

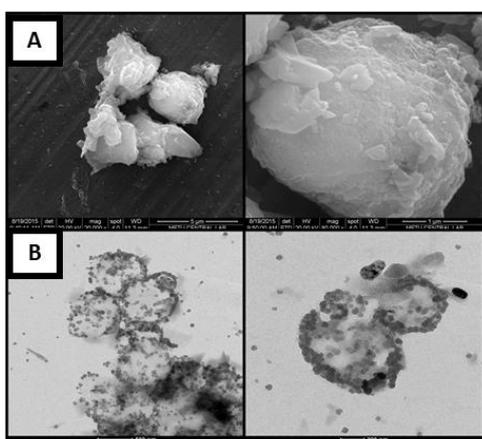
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Dual-drug delivery systems (DDDS), which are capable of controlling the release of multiple drugs, have recently become attractive topic since it allows the combined administration of different drugs and the optimization of their therapeutic effects. Advantages of DDDS such as different release periods and tunable dosages of active pharmaceutical agents, by enhancing their individual effects, make these systems smart materials and popular alternatives which can overcome the main challenges of conventional therapy systems. Nanoparticle or hydrogel-based DDDS have already been studied by several researchers. In our study, newly-developed self-assembled colloidal microcapsules were prepared to utilize them as DDDS. Colloidal microcapsules are one of the most interesting parts of these self-assembled structures whose shell side can be composed of several materials including nanoparticles. Layer-by-layer method (LbL) is one of the most used methods in the produce self-assembled structures. These self-assembled structures, independent from their single form, possess attractive properties such as high stability, enhanced functionality and increased loading capacity.

In this study, novel self-assembled colloidal microcapsules by using aminated positively charged PS particles and Ibuprofen crystals as core material and solid lipid nanoparticles (SLNs) as shell material were prepared. SLNs have been used as an alternative nanocarrier since the 1990s, which can be prepared by using various physiologically related lipids, emulsifiers and water. Due to their high biocompatibility, stability and availability, to encapsulate various active materials, SLNs are distinguished from other alternatives in the use of pharmaceuticals and biomedical applications. In this study ascorbic acid loaded SLNs were utilized. In addition to SLNs, gold nanoparticles (AuNPs) are also exploited as shell materials in order to benefit from their enhanced optical and biosensing properties.

The performance of establishing the layers was monitored by measuring the zeta-potential change. Also the self-assembled structures were visualized by SEM and TEM (Figure1). Controlled drug release from the microcapsules was monitored by using UV-vis. spectroscopy. Due to several advantageous properties such as being composed of physiologically related lipids, possessing properties like small and adjustable structure, high surface area, enhanced stability, stimuli-responsivity and increased encapsulation efficiency, these unique systems will be an ideal alternative to the conventional nanocarriers, which are especially used in pharmaceutical and biomedical applications as controlled drug delivery agents.



**Figure 1.** Colloidal Ibuprofen microcapsules prepared by using SLNs or AuNPs **A)** before and **B)** after core removal.

# General Physical Description of the Behavior of Oppositely Charged Polyelectrolyte/Surfactant Mixtures at the Air/Water Interface

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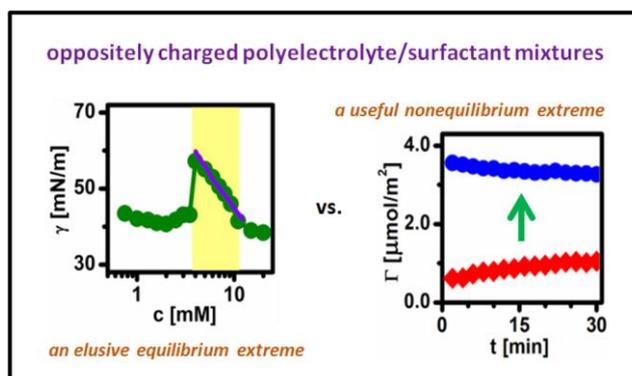
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We report the first unifying general physical description of the behavior of oppositely charged polyelectrolyte/surfactant mixtures at the air/water interface in terms of equilibrium vs. nonequilibrium extremes [1]. The poly(diallyldimethylammonium chloride)/sodium dodecyl sulfate (Pdadmac/SDS) system with added NaCl at two polyelectrolyte concentrations and the poly(sodium styrenesulfonate)/dodecyltrimethylammonium bromide (NaPSS/DTAB) system at two molecular weights have been systematically examined using a variety of bulk and surface techniques. A key aim was to resolve the controversy in the literature about the nature of the surface tension peak [2], which was found originally for the Pdadmac/SDS system but not the NaPSS/DTAB system [3], while later we found it for both systems [4].

Similarities in the general behavior of the systems are described. Following slow precipitation of aggregates in the equilibrium two-phase region, which can take several days or even weeks, depletion of surface-active material can result in the surface tension peak. The limiting time scale in the equilibration of the samples is the kinetics either of aggregate growth or settling. At the same time, aggregates may spontaneously dissociate and spread material in the form of a kinetically-trapped film if they interact with the interface, and a low surface tension then results out of equilibrium conditions. These interactions can occur while there remains a suspension of aggregates prior to full precipitation. Two clear differences in the behavior of the systems are the position in the isotherm of the surface tension peak and the time it takes to evolve. These features are both rationalized in terms of the nature of the bulk binding interactions.

The key nonequilibrium mechanisms that explain why reproducible steady state interfacial properties out of equilibrium conditions can be measured are thus set out systematically for the first time. We conclude the origin of the controversy about the surface tension peak: the original data on the NaPSS/DTAB system did not represent the assumed equilibrium after all.



**Figure 1** A schematic showing (left) the unexpected surface tension peak for the 17 kDa NaPSS/DTAB system and (right) spread films by exploiting aggregate spreading for the 100–200 kDa Pdadmac/SDS system.

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# Ex-Vivo Force Spectroscopy of Intestinal Mucosa

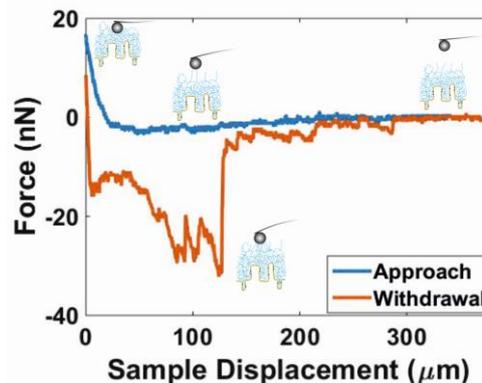
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Body cavities exposed to the external environment are lined by the so-called mucosal barriers i.e., one or more layers of mucus-covered epithelial cells overlying loose connective tissue, which act as the primary interface between the host and the physical environment. Mucus i.e., the viscous and hydrated gel that covers epithelial surfaces serves multiple purposes [1,2]. It is a lubricious barrier that protects the epithelium while keeping it hydrated. Nevertheless, mucus still allows, in an extremely selective manner, the diffusion of ions, nutrients and bacteria. Historically, most of the research on mucosal barriers has focused on the epithelial cells and on the underlying lymphoid tissues. In comparison, mucus has traditionally received much less attention. However, this tendency is changing. It is now well-established that many mucosa diseases e.g., cystic fibrosis, ulcerative colitis and even the propensity to certain infections, are related to dysfunctions of the mucus barrier [3]. Whether these dysfunctions are consequences or causes of the diseases, further research in this direction will increase our understanding on the corresponding etiology and could lead to novel therapeutic strategies. Mucus also plays a crucial role in mucosal drug delivery as it is the first barrier faced by drug delivery systems. While this aspect has been traditionally underestimated, the need for a deeper mechanistic understanding of mucus as a barrier to drug delivery is nowadays well-recognized [4]. The difficulty of performing in-vivo and ex-vivo mucus studies is probably behind the fact that mucus has been less investigated than the underlying mucosal layers. Because of technical limitations, mucus properties have mainly been addressed by in vitro studies. However, this approach can lead to artifacts as mucus collection can alter its structure. Here, we show how a standard Atomic Force Microscopy (AFM) setup can be modified to overcome this technical limitation allowing ex-vivo studies of mucosal tissues. The technique was applied to study the interactions between colloidal micro-particles and the mucosal surface of the distal part of the small intestine (ileum) collected from adult pigs. By studying ileum mucosa by means of AFM-based force spectroscopy (Fig. 1) we were able to quantify, at different pH values, its stiffness and adhesiveness. Additionally, we showed that the outer mucus blankets can give rise to bridging interactions that extend several hundreds of  $\mu\text{m}$  from their outer steric repulsive surface, and how this outer surface can absorb particles as big as  $15 \mu\text{m}$  i.e., more than one order of magnitude bigger than the mesh size typically reported for mucus mesh size [1].



**Figure 1** Representative force measurement on ileum mucosa in physiological conditions.

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# Near-wall velocimetry of complex fluids on a rheometer using evanescent wave dynamic light scattering

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Assessing the near wall velocity profile of complex fluids can be important in a number of situations, in particular in the context of the possible occurrence of slip at the wall. The interplay of mechanical properties of the fluid, hydrodynamic and chemico-physical interactions with the wall may result in discontinuities and non-adhesion of the fluid to the walls.

The advancement of relevant experimental techniques is then desirable. Here, we present the implementation and use of evanescent wave dynamic light scattering for near-wall velocimetry (in a range of 100 nm from surface) on a rotational rheometer. With this technique, we gain access to both a near-wall velocity as well as to the microscopic shear rate. The technique takes advantage of the penetration depth (order of 500nm) of light at total internal reflection to resolve the velocity gradient of colloidal tracers (220nm) in the penetration depth as well as the velocity of the slowest tracers nearest to the glass bottom plate of the rheometer. The tool can be relatively easily implemented on commercial rheometers. We describe the principles of the technique [1]. The abilities are demonstrated on simple Newtonian fluids, where no slip flows were observed. Further applications to complex fluids (colloidal suspensions and polymer solutions) are presented. Viscoelastic fluids were found to present near wall shear rate different from the macroscopic shear rate, and non-zero slip velocities and lengths. In particular the ability to detect the presence and onset of slip is shown in the case of Laponite and microgel dispersions and emulsions .

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# Bacterial adhesion to surfaces is accomplished by detachment and (re)-attachment of multiple, reversibly-binding tethers

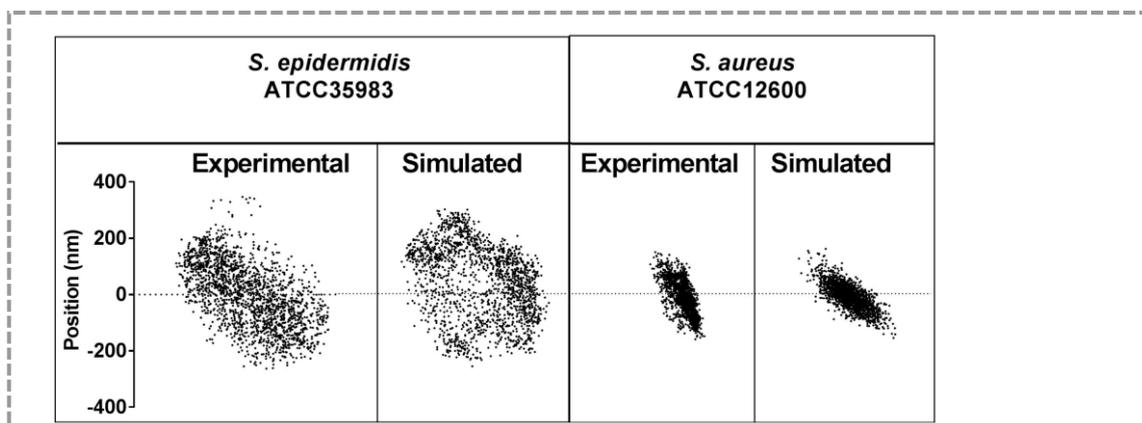
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Bacterial adhesion takes place ubiquitously and although initially adhering bacteria may detach within the first seconds, the adhesion gets irreversible within minutes as has been often observed [1]. By analyzing confined Brownian motion and performing AFM force-distance measurements with a bacterial probe we found a relationship between the amplitude of the nano-sized Brownian bacterial displacements and the bacterial adhesion-force. This suggests that bacteria adhere irreversibly to surfaces with a number of reversibly-binding tethers that can individually detach if the force that is associated with tether stretching is larger than the adhesion force. Detachment and re-attachment of individual tethers can subsequently give rise to additional bacterial displacements. Arguments that confirm this hypothesis build on the observation that AFM force-distance curves show detachment events and on the analysis of bacterial Brownian motion showing that over long time periods mean-squared-displacements increase. In order to further confirm our hypothesis we built a Monte Carlo model to simulate Brownian motion of adhering bacteria with a large number of reversibly-binding tethers. Simulation results indeed confirm that weakly binding tethers give rise to larger bacterial displacements than strongly binding tethers (see Fig. 1). This makes bacterial adhesion mechanistically comparable with the irreversible adsorption of high-molecular-weight proteins to surfaces mediated by multiple, reversibly-binding molecular segments [2].



**Figure 1** Experimentally observed position-maps representing XY-positions of the center of bacteria of two different strains at consecutive time points with a time interval of 0.015 s, as compared with *in silico* generated position-maps obtained by varying the tether adhesion force.

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# Amyloid- $\beta$ peptides aggregation and their interaction with raft-mimic model membranes

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A hallmark pathological feature of Alzheimer's disease (AD) is aggregation and deposition of  $\beta$ -Amyloid peptides ( $A\beta$ ) in the brain. Different complementary techniques have been applied to study the aggregation of different  $A\beta$  peptides, from monomers to fibrils, and their interaction with model membranes with biomimetic composition. Laser light scattering has been applied to investigate the early stages of  $A\beta$  peptides aggregation. Calorimetry and X-ray and neutron scattering have been used to investigate the effect of  $A\beta$  peptide interaction on the thermotropic and structural behavior of model membranes in bulk, while neutron reflectivity has been applied to study, with the Angstrom sensitivity, the structural interaction of peptides with complex membranes prepared by the Langmuir-Blodgett deposition technique. Peptide-membrane interaction was found to depend both on membrane composition and on the state of aggregation of the peptide. Moreover the N-terminal portion of  $A\beta$  was seen to interact with lipids of the bilayer probably promoting the penetration of peptide in the membrane.

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# Surfactant-free W/O emulsions for skin-care applications

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The potential of skin irritation by surfactants is well documented. Surfactants are usually needed for the creation of a stable water-in-oil (W/O) or oil-in-water (O/W) emulsion with small droplet sizes. Pickering emulsions could be made without surfactants, but they usually have very large droplet sizes which give rise to fast creaming or sedimentation.

A new way to stabilize W/O emulsions had been developed during the last years based on oil phases which show an increased uptake of water and transforming the oil phase into a liquid crystalline phase of high viscosity [1]. An oil phase that shows this possibility of formation of a liquid crystal when in contact with water may consist of monoglycerides like monolinolein, used in this work, or phytantriol. The challenges in this study are manifold. For skin care applications the oil phase must contain natural oils like almond oil, argan oil, borage seed oil etc. The common feature of all these skin function oils and mixtures thereof is that they contain many different molecular species and such polydisperse systems have a low tendency to form liquid crystalline phases.

The challenges in this project are manifold:

- Firstly, it is necessary to find a successful formulation that allows the formation of the desired liquid crystalline phase (preferentially a reverse hexagonal phase).
- Secondly, the aqueous phase must be finely dispersed in the oil phase to form droplets in the range a few micrometers only. During this process the oil phase – even though already in contact with the aqueous phase – must not yet form a liquid crystal. The latter would have a much too high viscosity to allow the dispersion of water into small droplets. This can be achieved by operating at temperatures above the melting temperature of the liquid crystal.
- Once the dispersion is formed the product must be quenched quickly below this melting temperature of the liquid crystalline oil phase in order to stabilize the dispersion and to prevent sedimentation, creaming or phase separation.

In this contribution examples for the successful formation of surfactant free W/O emulsions using mixtures of natural skin function oils will be presented. The melting temperature of the liquid crystalline phase, as determined by small-angle X-ray scattering, is in the range of about 50°C which guarantees good long-term stability. Also freezing and thawing cycles do not destroy the stability. These emulsions can be store at room temperature over many months.

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# Nanoscale mechanics of inclusions in lipid bilayers

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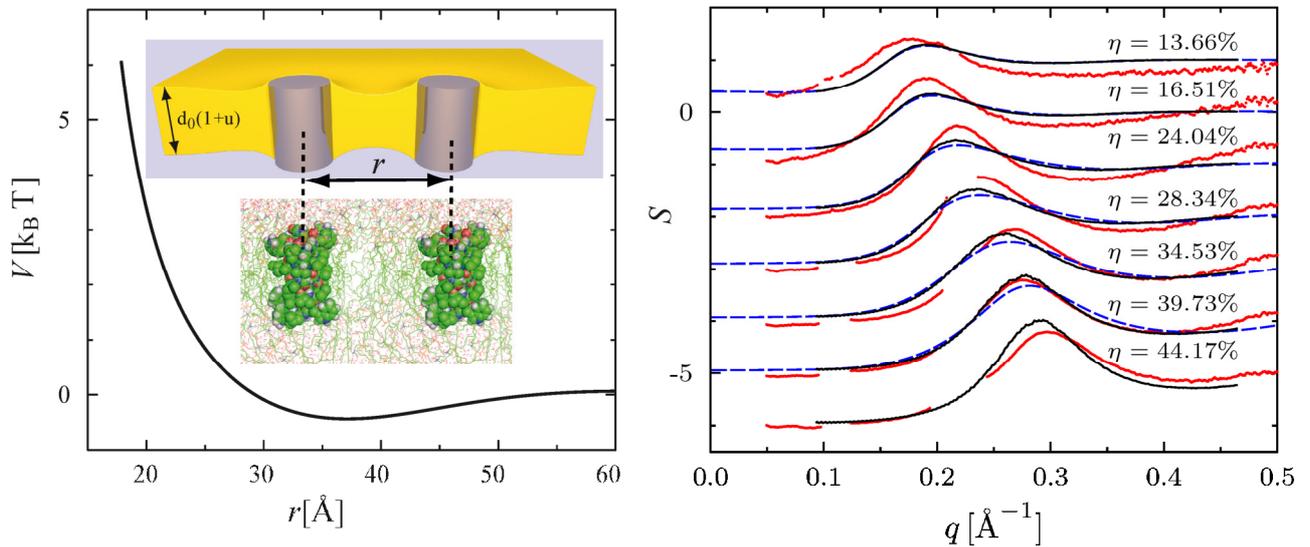
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As basic constituents of cell membranes, lipid bilayers play an important role in biological processes, not as a passive background, but rather as a medium that responds to and influences (albeit in a subtle way) the behavior of other membrane components, such as membrane proteins. The coupling between the lipid bilayer and these inclusions occurs by a deformation of the membrane in its entirety. Hence, one must describe it using conceptual schemes (e.g. elasticity theories) developed for the understanding of self-assembled systems. Since the deformation occurs over nanometer scales, both the acquisition of quantitative experimental information and the formulation of an appropriate model are challenging.

We use a complete elastic theory for the deformation [1] in order to determine the interaction potential between gramicidin channels in membranes by fitting small-angle X-ray scattering data recorded at varying channel concentration [2]. We extract the preferred slope at contact and its associated anchoring strength [3], thus answering a question that had remained open for twenty years. In phospholipid (DLPC) bilayers, the membrane thickness decreases with an angle of about 30° away from contact.

We confirm our results by predicting (with no adjustable parameters) numerical simulations for the interaction of gramicidin channels in other types of membranes as well as experimental conductivity data for the lifetime of the channels in DOPC, bringing together three completely different experimental techniques within one theoretical framework.



**Figure 1** Left: Interaction potential  $V(r)$  between two gramicidin channels in a DLPC membrane. The curve corresponds to our best fit of the experimental data. Inset: elastic model of the membrane, with the channels described as rigid cylinders; a more realistic representation is given below. Right: Structure factors  $S(q)$  for the same system at different surface fractions  $\eta$  of inclusions (red solid lines) and best fits using the interaction potential on the left. The fits are obtained via Monte Carlo simulations (solid black lines) or using the HNC approximation (dashed blue lines).

**Acknowledgements** The authors acknowledge financial support from the French Agence Nationale de la Recherche (Contract ANR-12-BS04-0023-MEMINT).

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# Controlling and Formation of Vesicle Based Polymeric Nanocapsules

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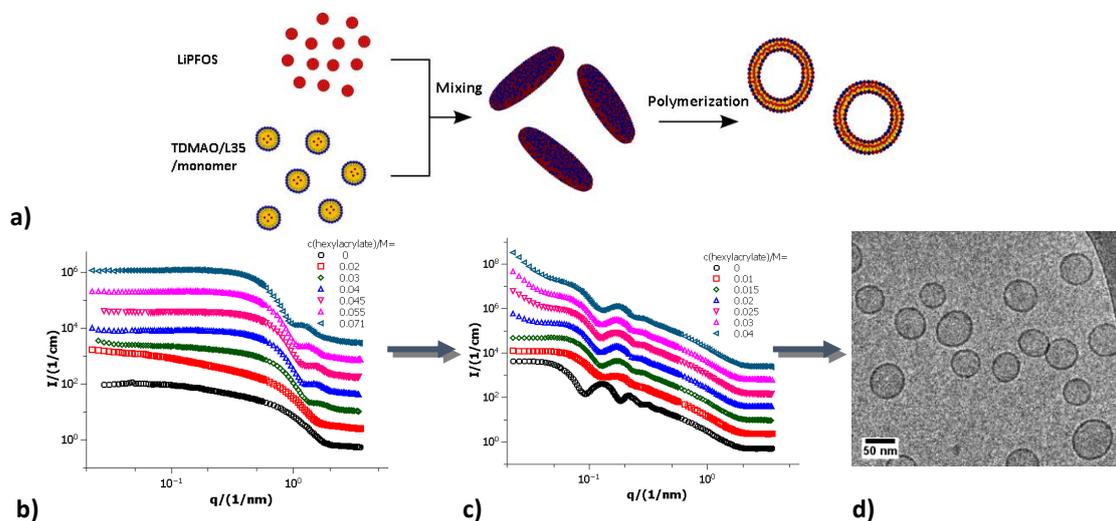
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Hollow polymer nanocapsules are appealing structures with their increasing usage in nanomedicine, based upon their structural advantage for encapsulating drugs, proteins or enzymes [1]. Nanocapsules were studied and developed formerly with utilization of self-aggregated templates through the stabilization of vesicle structures particularly via polymerization within the bilayer [2]. In our work we developed this concept further in order to produce monodisperse capsules of controllable size. A spontaneously formed well-defined vesicle system obtained by mixing of micellar TDMAO (tetradecyldimethylamine oxide) and LiPFOS (lithium perfluorooctylsulfonate) solutions, can be controlled precisely with respect to size and stability by the addition of the Pluronic type of copolymers (EO<sub>n</sub>-PO<sub>m</sub>-EO<sub>n</sub>) with a low polydispersity of 5% [3-4]. These kinetically stabilised vesicles are sufficient to be used as templates by fixing with polymerisation in order to form polymer nanocapsules. Therefore monomeric precursors were incorporated into the bilayer and eventually these structures were stabilized by UV induced radical polymerization using cross-linkers to ensure having a complete polymer network in the shell.

Structural transitions of the vesicles upon incorporation of the different monomers and the cross-linkers as well as the effect of subsequent polymerization in the membrane have been investigated by light scattering, small angle neutron scattering, electron microscopy and turbidity measurements. SANS experiments remark a noticeable transition from monomer loaded micellar system to vesicles and the following polymerization process shows that the initial structures can be successfully retained (Fig.1). Based on these results the potential of this approach to produce well-defined nanocapsules starting from a self-assembled system and subsequent polymerization is critically evaluated.



**Figure 1** a) Schematic representation of the synthesis of polymer nanocapsules b) SANS intensity patterns of monomer loaded micelles c) SANS intensity patterns of vesicles containing increasing amounts of monomer d) Cryo-TEM image of cross-linked polymerized nanocapsules.

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